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EPA METHOD STUDY 22

METHOD 612-CHLORINATED HYDROCARBONS

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The study design was based on Youden's plan for collaborative tests of analytical methods. Three Youden pair samples of the test compounds were spiked into six types of test waters and then analyzed. The test waters were distilled water, tap water, a surface water, and three different industrial wastewater effluents. The resulting data were statistically analyzed using the computer program entitled "Interlaboratory Method Validation Study" (IMVS). Using the mean recovery for each subject compound, the mean recoveries for the method were in the range of 64 to 90%. Overall precision was in the range of 26 to 41%, and single-analyst precision was in the range of 16 to 24%. In general, mean recoveries, overall standard deviation (S), and the single-analyst standard deviations (SR) were directly proportional to the true concentration levels. In all cases, there was no evidence of a statistically significant effect on accuracy or precision due to water type.

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FOREWORD

Environmental measurements are required to determine the quality of ambient waters and the character of waste effluents. The Environmental Monitoring and Support Laboratory (EMSL) - Cincinnati conducts research to:

- Develop and evaluate techniques to measure the presence and concentration of physical, chemical, and radiological pollutants in water, wastewater, bottom sediments, and solid waste.
- Investigate methods for the concentration, recovery, and identification of viruses, bacteria, and other microorganisms in water.
- Conduct studies to determine the responses of aquatic organisms to water quality.
- Conduct an agency-wide quality assurance program to assure standardization and quality control of systems for monitoring water and wastewater.

EPA Method Study 22, Method 612-Chlorinated Hydrocarbons reports the results of EPA's method study for the following priority pollutants:

hexachloroethane	1,3-dichlorobenzene
hexachlorobutadiene	1,4-dichlorobenzene
2-chloronaphthalene	1,2,4-trichlorobenzene
1,2-dichlorobenzene	hexachlorobenzene

Federal agencies, states, municipalities, universities, private laboratories, and industry should find this evaluative study of assistance in monitoring and controlling pollution in the environment.

Robert L. Booth
Director, EMSL-Cincinnati

ABSTRACT

An interlaboratory study in which 20 laboratories participated was conducted to provide precision and accuracy statements for the proposed EPA Method 612-Chlorinated Hydrocarbons for measuring concentrations of the Category 3 chemicals hexachloroethane, hexachlorobutadiene, 2-chloronaphthalene, 1,2-dichlorobenzene, 1,3-dichlorobenzene, 1,4-dichlorobenzene, 1,2,4-trichlorobenzene, hexachlorobenzene, and hexachlorocyclopentadiene in municipal and industrial aqueous discharges. Hexachlorocyclopentadiene was eliminated from the study because of its instability in the solvent used to prepare sample concentrates.

The study design was based on Youden's plan for collaborative tests of analytical methods. Three Youden pair samples of the test compounds were spiked into six types of test waters and then analyzed. The test waters were distilled water, tap water, a surface water, and three different industrial wastewater effluents. The resulting data were statistically analyzed using the computer program entitled "Interlaboratory Method Validation Study" (IMVS). Using the mean recovery for each subject compound, the mean recoveries for the method were in the range of 64 to 90%. Overall precision was in the range of 26 to 41%, and single-analyst precision was in the range of 16 to 24%. In general, mean recoveries, overall standard deviation (S), and the single-analyst standard deviations (SR) were directly proportional to the true concentration levels. In all cases, there was no evidence of a statistically significant effect on accuracy or precision due to water type.

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SECTION 1

INTRODUCTION

EPA first promulgated guidelines [1] establishing test procedures for the analysis of pollutants in 1973, following the passage of the Federal Water Pollution Control Act in 1972 by Congress. Pursuant to the amendment and publication of these guidelines, EPA entered into a Settlement Agreement--the Consent Decree--which required the study and, if necessary, regulation of 65 "priority" pollutants and classes of pollutants of known or suspected toxicity to the biota. Subsequently, Congress passed the Clean Water Act of 1977 [2], mandating the control of toxic pollutants discharged into ambient waters by industry.

In order to facilitate the implementation of the Clean Water Act, EPA selected for limited study 129 specific toxic pollutants, 113 organic and 16 inorganic. The organic pollutants were divided into 12 categories based on their chemical structure. Analytical methods were developed by EPA for these 12 categories through in-house and contracted research and may eventually be required for the monitoring of the 113 toxic pollutants in industrial wastewater effluents, as specified by the Clean Water Act of 1977.

This report describes the interlaboratory study of Method 612-Chlorinated Hydrocarbons which is proposed for the Category 3 chemicals: hexachloroethane, hexachlorobutadiene, 2-chloronaphthalene, 1,2-dichlorobenzene, 1,3-dichlorobenzene, 1,4-dichlorobenzene, 1,2,4-trichlorobenzene, hexachlorobenzene, and hexachlorocyclopentadiene. Hexachlorocyclopentadiene, one of the category compounds, was dropped from the method study because of its instability in the solvent used to prepare sample concentrates. The primary objective of the study was to characterize the behavior of Method 612-Chlorinated Hydrocarbons in terms of accuracy, overall precision, single-analyst precision, and effect of water type on accuracy and precision. The study was conducted with the cooperation of 20 participating laboratories under auspices of the Environmental Monitoring and Support Laboratory (EMSL)-Cincinnati. The participating laboratories, which were selected because of their technical capabilities and experience in trace analyses, are listed in Table 1.

The data were collected from the 20 laboratories according to Youden's [3] collaborative testing design. Formal statistical techniques compatible with the Youden design were used to identify outliers, estimate the method's accuracy and precision, and test for the effect of water type. The formal

statistical analyses were carried out using the Interlaboratory Method Validation Study (IMVS) computer program [4]. The information obtained from the statistical analyses was summarized and reduced to a descriptive form for the purpose of interpretation and presentation.

Method 612-Chlorinated Hydrocarbons was developed by IT Enviroscience under a contract with the Physical and Chemical Methods Branch, EMSL-Cincinnati. Method 612-Chlorinated Hydrocarbons is presented in Appendix B. Briefly, the method requires extraction of the pollutants with methylene chloride, solvent exchange, concentration by Kuderna-Danish, extract cleanup on activated Florisil®, and subsequent gas chromatographic (GC) analysis using electron capture (EC) detection.

TABLE 1. PARTICIPATING LABORATORIES

Carborundum Analytical Laboratory Sacramento, CA 95823	Radian Corporation Austin, TX 78758
EMS Laboratories Indianapolis, IN 46241	Southern Research Institute Birmingham, AL 35205
Enbionics/Poison Lab MetPath Companies Denver, CO 80222	Southwest Research Institute San Antonio, TX 78284
Environmental Research & Technology Westlake Village, CA 91361	Stewart Laboratories, Inc. Knoxville, TN 37921
Environmental Research & Technology Concord, MA 01742	Syracuse Research Corporation Syracuse, NY 13210
Environmental Science & Engineering, Inc. Gainesville, FL 32604	Systems, Science & Software LaJolla, CA 92038
Foremost Foods Company Research Center Dublin, CA 94556	Texas Instruments Dallas, TX 75265
Gulf South Research Institute New Iberia, LA 70560	Wilson Laboratories Saling, KS 67401
Jacobs Engineering Group Pasadena, CA 91105	U.S. EPA Environmental Monitoring & Support Laboratory Physical & Chemical Methods Branch Cincinnati, OH 45268
Lancaster Laboratories Lancaster, PA 17601	
Monsanto Research Corporation Dayton, OH 45407	

SECTION 2

SUMMARY

As a result of the collaborative study conducted and the data analysis, the following conclusions can be drawn concerning EPA Method 612-Chlorinated Hydrocarbons.

- The accuracy of the method could be expressed as a linear function of the true concentration. In the majority of the equations the slope of the line represents the percent recovery attributable to the method. The regression equations for accuracy are shown in Table 2.

- The precision of the method could be expressed as a linear function of the mean recovery. In the majority of the equations the slope represents the relative standard deviation attributable to the method, both as single-analyst and overall standard deviations. The regression equations for precision are also shown in Table 2.

- The average mean recovery at the six concentrations in the six water types for each compound compared well with data generated on distilled water and industrial effluents during the method development phase.

- Six water types were used in this study: distilled, tap, surface, and three relatively interference-free industrial effluents. No significant difference in method performance was attributable to the water type from which the analysis was performed.

- For all data for the eight compounds, 25% was rejected as determined by laboratory ranking and individual outlier tests. The data rejection was found to be nonuniform among laboratories. More than 82% of the rejected data was generated by eight of the 20 participating laboratories. Of the 20 participating laboratories, one had 98% of its total raw data rejected as outliers and nine laboratories had all of their raw data rejected for between one and four of the compounds studied in all water types.

- Some of the problems encountered in applying the method during this study included: One laboratory had trouble with the concentration of the extract using the Kuderna-Danish apparatus and some laboratories had to use peak height measurements for quantitation because occasional interference peaks in wastewaters created faulty integration when using recording integrators.

TABLE 2.

ENVIRONMENTAL MONITORING AND SUPPORT LABORATORY
OFFICE OF RESEARCH AND DEVELOPMENT
ENVIRONMENTAL PROTECTION AGENCY

EPA METHOD VALIDATION STUDY-IT ENVIROSCI CHTDRCARS

REGRESSION EQUATIONS FOR ACCURACY AND PRECISION FOR COMPOUNDS 1 - 4

WATER TYPE	HEXACHLOROETHANE	HEXACHLOROBUTADIENE	2-CHLORONAPHTHALENE	1,2-DICHLOROBENZENE
APPLICABLE CONC. RANGE	(1.02 - 14.80)	(3.12 - 36.80)	(19.10 - 268.00)	(29.80 - 356.00)
DISTILLED WATER				
SINGLE-ANALYST PRECISION	SR = 0.23X + 0.07	SR = 0.18X + 0.08	SR = 0.28X - 1.17	SR = 0.22X - 2.95
OVERALL PRECISION	S = 0.36X - 0.00	S = 0.53X - 0.12	S = 0.38X - 1.39	S = 0.41X - 3.92
ACCURACY	X = 0.74C - 0.02	X = 0.61C + 0.03	X = 0.75C + 3.21	X = 0.85C - 0.70
TAP WATER				
SINGLE-ANALYST PRECISION	SR = 0.33X - 0.10	SR = 0.29X - 0.23	SR = 0.16X + 0.25	SR = 0.17X +10.94
OVERALL PRECISION	S = 0.34X - 0.04	S = 0.42X + 0.14	S = 0.26X - 0.71	S = 0.31X + 5.35
ACCURACY	X = 0.78C - 0.09	X = 0.64C + 0.18	X = 0.74C + 3.41	X = 0.87C + 6.70
SURFACE WATER				
SINGLE-ANALYST PRECISION	SR = 0.17X + 0.51	SR = 0.30X + 0.05	SR = 0.13X + 0.92	SR = 0.30X - 4.00
OVERALL PRECISION	S = 0.46X + 0.07	S = 0.39X - 0.06	S = 0.18X + 1.20	S = 0.32X - 2.18
ACCURACY	X = 0.83C + 0.06	X = 0.62C + 0.12	X = 0.77C + 3.67	X = 0.81C + 0.44
WASTE WATER 1				
SINGLE-ANALYST PRECISION	SR = 0.24X - 0.05	SR = 0.25X + 0.21	SR = 0.12X +14.77	SR = 0.13X + 4.87
OVERALL PRECISION	S = 0.26X + 0.07	S = 0.37X + 0.02	S = 0.24X + 8.18	S = 0.28X + 4.26
ACCURACY	X = 0.80C + 0.05	X = 0.66C + 0.08	X = 0.74C +11.64	X = 0.85C - 0.52
WASTE WATER 2				
SINGLE-ANALYST PRECISION	SR = 0.25X + 0.03	SR = 0.25X + 0.44	SR = 0.12X + 8.51	SR = 0.22X + 1.60
OVERALL PRECISION	S = 0.45X - 0.09	S = 0.39X + 0.39	S = 0.27X + 2.91	S = 0.34X - 0.63
ACCURACY	X = 0.73C - 0.03	X = 0.63C + 0.39	X = 0.72C + 7.64	X = 0.83C + 3.41
WASTE WATER 3				
SINGLE-ANALYST PRECISION	SR = 0.20X - 0.05	SR = 0.18X + 0.14	SR = 0.14X + 2.92	SR = 0.21X + 2.78
OVERALL PRECISION	S = 0.27X - 0.03	S = 0.38X - 0.06	S = 0.26X + 2.79	S = 0.32X + 0.77
ACCURACY	X = 0.81C - 0.13	X = 0.71C + 0.31	X = 0.74C + 2.55	X = 0.87C + 5.53

X = MEAN RECOVERY
C = TRUE VALUE FOR THE CONCENTRATION

TABLE 2. (CONTINUED)

ENVIRONMENTAL MONITORING AND SUPPORT LABORATORY
OFFICE OF RESEARCH AND DEVELOPMENT
ENVIRONMENTAL PROTECTION AGENCY

EPA METHOD VALIDATION STUDY-IT ENVIROSCI CHTDRCARS

REGRESSION EQUATIONS FOR ACCURACY AND PRECISION FOR COMPOUNDS 5 - 8

WATER TYPE	1,3-DICHLOROBENZENE	1,4-DICHLOROBENZENE	1,2,4-TRICHLOROBENZENE	HEXACHLOROBENZENE
APPLICABLE CONC. RANGE	(20.40 - 238.00)	(23.00 - 324.00)	(15.10 - 216.00)	(1.29 - 14.90)
DISTILLED WATER				
SINGLE-ANALYST PRECISION	SR = 0.21X - 1.03	SR = 0.16X - 0.48	SR = 0.23X - 0.44	SR = 0.14X + 0.07
OVERALL PRECISION	S = 0.49X - 3.98	S = 0.35X - 0.57	S = 0.40X - 1.37	S = 0.36X - 0.19
ACCURACY	X = 0.72C + 0.87	X = 0.72C + 2.80	X = 0.76C + 0.98	X = 0.87C - 0.02
TAP WATER				
SINGLE-ANALYST PRECISION	SR = 0.23X + 2.91	SR = 0.20X + 2.80	SR = 0.15X + 0.60	SR = 0.22X - 0.08
OVERALL PRECISION	S = 0.35X + 2.65	S = 0.26X + 5.88	S = 0.30X + 0.72	S = 0.32X - 0.14
ACCURACY	X = 0.79C + 4.02	X = 0.75C + 4.15	X = 0.68C + 1.97	X = 0.92C - 0.08
SURFACE WATER				
SINGLE-ANALYST PRECISION	SR = 0.17X - 0.16	SR = 0.17X + 5.13	SR = 0.16X + 0.75	SR = 0.08X + 0.13
OVERALL PRECISION	S = 0.26X - 1.04	S = 0.42X + 0.22	S = 0.43X + 0.42	S = 0.22X - 0.01
ACCURACY	X = 0.75C + 0.55	X = 0.73C + 5.56	X = 0.74C + 2.40	X = 0.97C - 0.06
WASTE WATER 1				
SINGLE-ANALYST PRECISION	SR = 0.16X - 0.47	SR = 0.24X - 0.81	SR = 0.39X - 1.97	SR = 0.11X + 0.19
OVERALL PRECISION	S = 0.34X + 0.03	S = 0.25X + 4.30	S = 0.42X - 1.05	S = 0.18X + 0.16
ACCURACY	X = 0.78C + 4.47	X = 0.77C + 2.06	X = 0.75C + 0.70	X = 0.87C + 0.17
WASTE WATER 2				
SINGLE-ANALYST PRECISION	SR = 0.19X + 2.61	SR = 0.19X + 1.11	SR = 0.26X - 0.81	SR = 0.25X - 0.18
OVERALL PRECISION	S = 0.39X + 0.22	S = 0.34X + 1.80	S = 0.31X + 0.33	S = 0.39X + 0.16
ACCURACY	X = 0.75C + 1.34	X = 0.78C + 2.25	X = 0.80C - 0.21	X = 0.99C + 0.09
WASTE WATER 3				
SINGLE-ANALYST PRECISION	SR = 0.15X + 0.58	SR = 0.23X - 1.94	SR = 0.15X + 1.52	SR = 0.24X - 0.04
OVERALL PRECISION	S = 0.32X - 0.13	S = 0.34X - 3.58	S = 0.34X - 0.71	S = 0.38X + 0.03
ACCURACY	X = 0.71C + 2.52	X = 0.78C + 1.72	X = 0.78C + 2.11	X = 0.83C + 0.07

X = MEAN RECOVERY
C = TRUE VALUE FOR THE CONCENTRATION

SECTION 3

DESCRIPTION OF STUDY

The interlaboratory study design was based on Youden's plan [3] for collaborative evaluation of precision and accuracy for analytical methods. According to Youden's design, samples are analyzed in pairs at similar, but distinctly different concentrations. The analyst is requested to do only a single analysis for each sample and report only one value as in normal routine use of the method.

SELECTION OF LABORATORIES

Over 60 laboratories throughout the United States were asked by telephone about their interest and experience in this type of interlaboratory study. Approximately 40 bid packages were sent to interested laboratories, and these packages included a request for a price quote and information on their capabilities in trace organic analysis of wastewater. From the 36 bids received, 19 laboratories were selected because of their technical capabilities and experience in this area. Three volunteer laboratories from within the EPA initially were part of the program, but two of them dropped from the project because of other work demands. The total interlaboratory study therefore included 20 laboratories.

PREPARATION OF AMPULS

Separate stock solutions of each analyte were prepared for each ampul concentration by dissolving precisely weighed amounts of reagent grade, or better, quality of the eight chlorinated hydrocarbons in distilled in glass grade methyl ethyl ketone. Appropriate volumes of the stock solutions were mixed and diluted in 2000-mL volumetric flasks. The flasks were refrigerated overnight at 4°C. The following day, approximately 3-mL of the refrigerated solution was transferred into 5-mL glass ampuls using an all-glass or Teflon® delivery system. After the ampuls were cooled in a freezer at -30°C for three hours, they were sealed by a professional glass blower using the pull-and-twist technique.

When diluted to volume in the water type according to the instructions, the samples contained the concentrations of the chlorinated hydrocarbons shown in Table 3.

TRUE VALUE AND STABILITY OF CONCENTRATES

An important segment of this study was to verify the true values and stability of the chlorinated hydrocarbons in the methyl ethyl ketone concen-

TABLE 3. TRUE VALUES FOR CHLORINATED HYDROCARBONS (ug/L IN WATER)

Compound	Ampul 1	Ampul 2	Ampul 3	Ampul 4	Ampul 5	Ampul 6
Hexachloroethane	1.02	2.56	12.8	14.8	2.96	1.18
Hexachlorobutadiene	3.12	23.4	32.2	36.8	27.6	3.68
2-Chloronaphthalene	21.4	161.	268.	238.	143.	19.1
1,2-Dichlorobenzene	29.8	149.	298.	356.	178.	35.6
1,3-Dichlorobenzene	20.4	51.0	204.	238.	59.4	23.8
1,4-Dichlorobenzene	23.0	172.	288.	324.	194.	26.0
1,2,4-Trichlorobenzene	15.1	37.8	188.	216.	43.2	17.3
Hexachlorobenzene	1.49	7.44	14.9	12.9	6.46	1.29

*The true value stated for a parameter is the actual value calculated by weight for that parameter. Subsequent analyses were for verification only.

trates before they were used in the study. To achieve this verification, three replicate ampuls were randomly selected from each concentrate level and analyzed by triplicate injection into a gas chromatograph equipped with a recording integrator. To check stability these analyses were carried out at 0, 45, and 90 days after the ampuls were sealed and before the study was started. All concentrate values determined experimentally were within instrumental error of the calculated true values. The results of the stability and verity study are presented in Table A-1 to A-3 of the appendix.

PRELIMINARY STUDY

Previous EPA method studies have shown that more realistic results can be obtained if all participants fully understand the analytical and sample handling procedures before undertaking the full study. To familiarize the analyst with the analytical method and handling procedures, each of the 20 laboratories was sent a low-level Youden pair of sample concentrates, different from those to be used in the actual study, for spiking distilled water. Instructions, a copy of the method, and data report sheets were included.

The results of these analyses were collected, statistically analyzed, and discussed with the laboratories' representatives at a one-day conference meeting at EPA-Cincinnati. The meeting also allowed discussion of analytical problems and clarification of any methodology procedures. A summary of the preliminary data is presented in Table A-4 of the appendix.

The only major problem discussed at the prestudy conference was the difficulty encountered by the laboratories in achieving proper separation of the compounds using the commercially available GC column packings. IT Enviroscience had become aware of the problem earlier during the preliminary study and was working with the vendor to find a solution to the column-packing production problems. After the preliminary study conference each of the laboratories was sent a new GC column packing for chlorinated hydrocarbons, which would allow more reproducible separation of the components. The new packing, 1.5% OV-1/2.4% OV-225 on 80/100 mesh Supelcoport®, was made by Supelco, Inc., by chemical blending to give better reproducibility than their previous column packing materials.

ACTUAL METHOD VALIDATION STUDY

A summary of the test design using Youden's nonreplicate technique based on pairs with slightly dissimilar analyte concentrations is given below:

1) Twenty laboratories were sent three Youden pairs in sealed glass ampuls containing various levels of the eight chlorinated hydrocarbons in methyl ethyl ketone.

2) When the analyst was ready to start the analyses, the ampuls were opened and aliquots added to the appropriate water types according to instructions.

3) Each sample (ampul) was analyzed only once.

4) The six water types were analyzed with and without spiking, and the added level of constituent was determined by difference and reported as µg/L in each water type.

5) The three levels of chlorinated hydrocarbons used in the study were within the working range of the method and represented the range of levels one would normally expect to encounter in application of the method to real-world samples.

DESCRIPTION AND DISTRIBUTION OF SAMPLES

The individual laboratories provided their own samples of laboratory-distilled water, tap water, and a local surface water. The surface waters utilized in the study by the laboratories are listed in Table 4. The drinking waters were from the individual laboratory taps. The sources of wastewater effluent samples provided by IT Enviroscience are described as follows:

1) Wastewater No. 1 - Effluent from an industrial waste treatment system, including primary and secondary activated sludge treatment, followed by lagooning for up to 90 days. Wastewater source is large producer of organic chemicals, including intermediates, pesticides, and plastics, with several chlorinated benzenes, phenol, and chlorinated phenols produced or handled.

2) Wastewater No. 2 - Effluent from an industrial primary and secondary activated sludge treatment system followed by tertiary activated carbon treatment. Wastewater source is a large producer of inorganic and organic chemicals, including chemical intermediates and chlorinated and nitrated pesticides, with several Category 3 compounds produced or used as raw materials.

3) Wastewater No. 3 - Effluent from an industrial primary and secondary activated sludge treatment system combined with once-through cooling water and steam-stripped process wastewater. Wastewater source is a medium-size chemical plant specializing in basic chemicals (chlorine, caustic soda, chlorinated solvents, intermediate organics, and plastics).

The three wastewater types represented three industrial plant effluents on which the method was intended to be utilized.

The wastewater samples were collected as grab samples in 55-gallon stainless steel drums which had been precleaned with acetone, methylene chloride, and distilled water. Upon receipt by IT Enviroscience, the unfiltered wastewater samples were mixed and transferred into 1-quart bottles using an all Teflon system and stored in a refrigerator at 4°C until shipment to the laboratories.

After a laboratory demonstrated satisfactory separation of the compounds with the new GC column packing, it was sent 36 ampul concentrates (six sets of three Youden pairs), seven quart bottles each of three industrial

TABLE 4. SOURCES OF SURFACE WATERS USED IN THE STUDY

Water Source	Location
Bayou Teche	New Iberia, LA
Cahaba River	Birmingham, AL
Cherry Creek	Denver, CO
Duck Creek	Garland, TX
Eagle Creek Reservoir	Indianapolis, IN
Horn Pond	Woburn, MA
Hogtown Creek	Gainesville, FL
Glendale Reservoir	Glendale, CA
Great Miami River	Dayton, OH
Ohio River	Cinninnati, OH
Onondega Lake	Syracuse, NY
Sacramento River	Before Confluence of American River, CA
San Pedro Springs	San Antonio, TX
Smoky Hill River	Salina, KS
South Bay Aquaduct	San Francisco, CA
Susquehanna River	Lancaster, PA
Tennessee River	Knoxville, TN
Los Pana Squitos	Sorrento Valley, CA
Barton Springs Creek	Austin, TX
West Lake	Westlake Village, CA

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effluent types, instructions, and data report sheets. The wastewater samples were packed in ice in coolers and sent by air freight to minimize sample change and assure comparability of the wastewaters from laboratory to laboratory.

Figures A-1 through A-10 (in Appendix A) are chromatograms of the clean water and three wastewaters before and after spiking.

ANALYSIS AND REPORTING

A water spiking technique involving a water-soluble solvent concentrate (methyl ethyl ketone is approximately 28% soluble in water) was used in this study. Each analyst was instructed to add separate 2.0 mL aliquots of each concentrate to the bottle containing approximately 1 L of water or wastewater. The spiked sample was to be stirred for 15 minutes and then handled as a sample per the method. The results of the method's measurement for each constituent (in micrograms per liter of water) were then corrected by subtracting any blank sample reading and reported on data sheets by ampul and water type. The method utilized by the participating laboratories, Method 612-Chlorinated Hydrocarbons, is presented in Appendix B. There were no reported deviations.

IT Enviroscience reviewed the data for completeness and abnormal results. The data were then entered into the computer for statistical treatment. Any laboratory reporting unusually high or low data was requested to review its data for any possible errors in calculation but was not told how the reported data varied from the true values.

TREATMENT OF DATA

The objective of this interlaboratory study was to obtain information about the accuracy and precision associated with measurements generated by Method 612-Chlorinated Hydrocarbons. This objective was met through the use of statistical analysis techniques designed to extract and summarize the relevant information about accuracy and precision from the data reported by the participating laboratories. The statistical techniques are similar to the techniques recommended in the ASTM Standard Practice D2777-77.

The algorithms required to perform the statistical analyses have been integrated into a system of computer programs referred to as IMVS. The analyses performed by IMVS [4] include several tests for the rejection of outliers (laboratories and individual data points), summary statistics by concentration level for mean recovery (accuracy), overall and single-analyst standard deviation (precision), determination of the linear relationship between mean recovery and concentration level, determination of the linear relationship between the precision statistics and mean recovery, and a test for the effect of water type on accuracy and precision.

A detailed description of each of the statistical analysis procedures is presented below.

Rejection of Outliers

Spurious data points are always a part of any set of data collected during an interlaboratory test program. It is important to identify and remove these data points because they can lead to values of summary statistics which are not representative of the general behavior of the method. However, some erratic behavior in the data may be directly related to some facet of the method under the study. Therefore, spurious data points should not be removed indiscriminately, and any points that are removed should be clearly identified since further investigation of the analytical conditions related to the outliers might be of value. Data rejected as outliers for this study as a result of any of the folowing tests for outliers have been identified by the symbol "*" in the raw data tables.

Youden's Laboratory Ranking Procedure

In some cases the analytical values reported by a specific laboratory are so consistantly high or low that a large systematic error may be attributed to that laboratory. These data are not representative of the method and should be rejected. Youden's [3] ranking test for outlying laboratories was applied separately to data from each of the waters used in this study. Since six water types were used in this study, the laboratory ranking procedure was applied to these six different subsets of the data. Each laboratory ranking test was performed at the 5 % level of significance.

The Youden laboratory ranking procedure requires a complete set of data from every laboratory within a given water type. Missing data from laboratory i for water type j were replaced by the following procedure. Letting X_{ijk} denote the reported measurement from laboratory i for water type j and concentration level C_k, it is assumed that

$$X_{ijk} = \beta_j \cdot C_k^{\gamma_j} \cdot L_i \cdot \varepsilon_{ijk}$$

where β_j and γ_j are fixed parameters which determine the effect of water type j, L_i is the systematic error due to laboratory i and ε_{ijk} is the random within laboratory error. Taking natural logarithms, it follows that

$$\ln X_{ijk} = \ln \beta_j + \gamma_j \ln C_k + \ln L_i + \ln \varepsilon_{ijk}$$

which is a linear regression model with dependent variable $\ln X_{ijk}$ and independent variable $\ln C_k$. Details and justification for this model are discussed in the section "Comparison of Accuracy and Precision Across Water Types."

The natural logarithms of the individual laboratory's data were regressed against the natural logarithms of the true concentration levels for the six ampuls in each water type. The predicted values $\ln \hat{X}_{ijk}$ were obtained from the regression equation, and the missing values for X_{ijk} were estimated by $X_{ijk} = \exp(\ln \hat{X}_{ijk})$ where exp (X) denotes the constant e raised to the power X.

If the ranking test rejected a laboratory for a specific water type, then all of the laboratory's data for that water type were rejected as

outliers. The rejected values were excluded from all the remaining analyses. In addition, after completion of the laboratory ranking procedure, the predicted values created to fill in for the missing data were rejected and excluded from furtner analyses for all laboratories.

Test for Individual Outliers

The data remaining after the laboratory ranking procedure were grouped by water type. For each water type, the data were broken down into six subsets defined by the six concentration levels (ampuls) used in the study. For each subset of the data, all missing, zero, "less than" and "nondetect" data were rejected. Next, the test for individual outliers constructed by Thompson [5], and suggested in the ASTM Standard Practice D2777-77, was applied to the data using a 5% significance level. If an individual data point was rejected based on this test, it was removed from the subset, and the test was repeated using the remaining data in the subset. This process was continued until no additional data could be rejected.

STATISTICAL SUMMARIES

Summary statistics were calculated using the data remaining for each concentration level after the outlier rejection tests were performed. These summary statistics include: the number of retained data points, the mean recovery, accuracy as a percent relative error, the absolute overall standard deviation, the percent relative overall standard deviation, the absolute single-analyst standard deviation, and the percent relative single-analyst standard deviation. The basic formulae used to calculate these statistics are presented below where X_1, X_2...., X_n denote the values of the n retained data points for a specific concentration level:

Mean Recovery (X):

$$X = \frac{1}{n} \sum_{i=1}^{n} X_i$$

The usual concentration notation for mean recovery is $\overline{X}$; however, the symbol X is used in this report to be consistent with the IMVS output.

Accuracy as a % Relative Error:

$$\%RE = \frac{X - \text{True Value}}{\text{True Value}} \times 100$$

Overall Standard Deviation:

$$S = \sqrt{\frac{1}{n-1} \sum_{i=1}^{n} (X_i - X)^2}$$

and

Percent Relative Overall Standard Deviation:

$$\%RSD = \frac{S}{X} \times 100$$

The overall standard deviation S indicates the precision associated with measurements generated by a group of laboratories. This represents the broad variation in the data collected in an interlaboratory study. However, a measure of how well an individual analyst can expect to perform in his own laboratory is another important measure of precision. This single-analyst precision, denoted by SR, was estimated for each Youden pair by

$$SR = \sqrt{\frac{1}{2(m-1)} \sum_{i=1}^{m} (D_i - \bar{D})^2}$$

where

m = the number of complete sets of Youden pair observations remaining after outliers have been removed,

D_i = the difference between the observations in the ith Youden pair

and

$\bar{D}$ = average of the D_i values.

The percent relative single-analyst standard deviation was calculated by

$$\%RSD\text{-}SR = \frac{SR}{X^*} \times 100$$

where X^* is the average of the two mean recovery statistics corresponding to the two concentration levels defining the particular Youden pair.

These summary statistics provide detailed information on the accuracy and precision of the data obtained for each concentration level. One objective of the statistical analysis of the data is to summarize the information about accuracy and precision which is contained in the statistics.

It is often the case that a systematic relationship exists between the mean recovery (X) and the true concentration level (C) of the analyte in the sample. In addition, there are often systematic relationships between the precision statistics (S and SR) and the mean recovery (X). Usually these systematic relationships can be adequately approximated by a linear relationship (i.e. a straight line). Once these straight lines are established, they can be used to conveniently summarize the behavior of the method within a water type, and they can aid in comparing the behavior of the method across water types. In addition they can be used to obtain estimates of the accuracy and precision at any concentration level within the applicable range studied. They can also be used to predict the behavior of the method when used under similar conditions. These important relationships are discussed below.

STATEMENT OF METHOD ACCURACY

The accuracy of the method is characterized by the relationship of the mean recovery (X) to the true concentration (C) of the analyte in the water sample. In order to obtain a mathematical expression for this relationship, a regression line of the form

$$X = a + b \cdot C \qquad (1)$$

was fitted to the data by regression techniques.

It is often the case that the true concentration values vary over a wide range. In such cases, the mean recovery statistics associated with the larger concentration values tend to dominate the fitted regression line producing relatively larger errors in the estimates of mean recovery at the lower concentration values. In order to eliminate this problem, a weighted least squares technique was used to fit the mean recovery data to the true concentration values. The weighted least squares technique was performed by dividing both sides of Equation (1) by C resulting in Equation (2).

$$\frac{X}{C} = a \cdot \frac{1}{C} + b \quad . \qquad (2)$$

The (X/C) values were regressed against the (1/C) values using ordinary least squares to obtain estimates for the values of a and b. (This is equivalent to performing a weighted least squares with weights $w = 1/C^2$; see Reference [6], page 108 for details.) Equation (2) can easily be converted to the desired relationship given by Equation (1). The intercept (b) from Equation (2) becomes the slope (b) for Equation (1) and the slope (a) from Equation (2) becomes the intercept (a) for Equation (1). Equation (1) can be used to calculate the percent recovery over the applicable range of concentrations used in the study.

The percent recovery is given by

$$\text{Percent Recovery} = \left[\frac{a + b \cdot C}{C}\right] \times 100 = \left[\frac{a}{C} + b\right] \times 100 \qquad (3)$$

If the absolute value of the ratio (a/C) is small relative to the slope (b) for concentrations in the low end of the range of concentration levels used in the study, then the percent recovery can be approximated by b X 100. For example, suppose the true concentration values range from 25 µg/L to 515 µg/L, the fitted line is given by $X = -0.20 + 0.85 \cdot C$. The percent recovery would be approximated by $(0.85) \times 100 = 85\%$ over the specified range of 25 µg/L to 515 µg/L.

If the ratio (a/C) is not small relative to the slope (b), then the percent recovery depends upon the true concentration (C), and it must be evaluated at each concentration value within the specified range.

STATEMENT OF METHOD PRECISION

The precision of the method is characterized by the relationships between precision statistics (S and SR) and mean recovery (X). In order to obtain a mathematical expression for these relationships, regression lines of the form

$$S = d + e \cdot X \tag{4}$$

and

$$SR = f + g \cdot X^* \tag{5}$$

were fitted to the data.

As discussed previously with respect to accuracy, the values of X and X* often vary over a wide range. In such cases the standard deviation statistics associated with the larger mean recovery values will dominate the regression lines. This will produce relatively larger errors in the estimates of S and SR at the lower mean recovery values. Therefore, a weighted least squares technique was also used to establish the values of the parameters d, e, f, and g in Equations (4) and (5). The weighted least squares technique was performed by dividing both sides of Equation (4) by X resulting in Equation (6)

$$\frac{S}{X} = d \cdot \frac{1}{X} + e \tag{6}$$

and by dividing both sides of Equation (5) by X* resulting in Equation (7)

$$\frac{SR}{X^*} = f \cdot \frac{1}{X^*} + g \quad . \tag{7}$$

The (S/X) values were regressed against the (1/X) values and the (SR/X*) values were regressed against the (1/X*) values using ordinary least squares to obtain estimates for the parameters d, e, f, and g.

Equations (4) and (5) were obtained from Equations (6) and (7) in a manner similar to that discussed for mean recovery. The slope (d) for Equation (6) is the intercept (d) for Equation (4), and the intercept (e) for Equation (6) is the slope (e) for Equation (4). Similarly, the slope (f) for Equation (7) is the intercept (f) for Equation (5), and the intercept (g) for Equation (7) is the slope (g) for Equation (5).

Given Equations (4) and (5), the percent relative overall standard deviation and the percent relative single-analyst standard deviation are

$$\%RSD = \left[\frac{d}{X} + e\right] X\ 100 \tag{8}$$

and

$$\%RSD\text{-}SA = \left[\frac{f}{X^*} + g\right] X\ 100 \qquad (9)$$

respectively. If the absolute value of the ratio (d/X) is small relative to the slope (e), then the percent relative overall standard deviation can be approximated by (e X 100) over the applicable range of mean recovery values. Similarly if the ratio (f/X*) is small relative to the slope (g), then the percent relative single-analyst standard deviation can be approximated by (g X 100) over the applicable range of mean recovery values.

If the ratios (d/X) and (f/X*) are not small relative to the slopes (e) and (f), then the percent relative standard deviations depend upon the values of the mean recovery statistics X and X*, and they should be evaluated separately for each value of X and X*.

COMPARISON OF ACCURACY AND PRECISION ACROSS WATER TYPES

It is possible that the accuracy and precision of Method 612-Chlorinated Hydrocarbons depend upon the type of water being analyzed. The summary statistics X, S, and SR are calculated separately for each concentration level within each water type. They can be compared across water types in order to obtain information about the effects of water type on accuracy and precision. However, the use of these summary statistics in this manner has several disadvantages. First, it is cumbersome since there are 36 mean recovery statistics (X) (six concentrations X six waters), 36% statistics (S) and 18 precision statistics (SR) calculated for each compound. Comparison of these statistics across concentation levels and across water types becomes unwieldy. Second, the statistical properties of this type of comparisons procedure are difficult to determine. Finally, due to variation associated with X, S, and SR, comparisons based on these statistics can lead to inconsistent conclusions about the effect of water type. For example, distilled water may produce a significantly lower value than surface water for the precision statistic S at a high concentration, but a significantly higher value for S at a low concentration.

An alternative approach, described in detail in [7], has been developed to test for the effects of water type. This alternative approach is based on the concept of summarizing the average effect of water type across concentration levels rather than studying the local effects at each concentration level. If significant differences are established by this alternative technique, then the summary statistics can be used for further local analysis.

The test for the effect of water type is based on the following statistical model. If S_{ijk} denotes the measurement reported by laboratory i, for water type j, and ampul k; then

$$X_{ijk} = \beta_j \cdot C_k^{\gamma_j} \cdot L_i \cdot \varepsilon_{ijk} \quad \cdot \quad \begin{matrix} i = 1,2,\ldots, n \\ j = 1,2,\ldots, 6 \\ k = 1,2,\ldots, 6 \end{matrix} \qquad (10)$$

The model components β_j and γ_j are fixed parameters which determine the effect of water type j on the behavior and observed measurements (X_{ijk}). The parameter C_k is the true concentration level associated with ampul k. The model component L_i is a random factor which accounts for the systematic error associated with laboratory i. The model component ε_{ijk} is the random factor which accounts for the within laboratory error.

The model is designed to approximate the global behavior of the data. The multiplicative structure was chosen because of two important properties. First, it allows for a possible curvilinear relationship between the data (X_{ijk}) and the true concentration level C_k through the use of the exponent γ_j on C_k This makes the model more flexible in comparison to straight line models. Second, as will be seen below, there is an inherent increasing relationship between the variability in the data and the concentration level C_k in this model. This property is important because it is typical of interlaboratory data collected under conditions where the true concentration levels vary widely.

Accuracy is related directly to the mean recovery or expected value of the measurements (X_{ijk}). The expected value for the data modeled by Equation (10) is

$$E(X_{ijk}) = \beta_j \cdot C_k^{\gamma_j} \cdot E(L_i \cdot \varepsilon_{ijk}) \qquad (11)$$

Precision is related to the variability in the measurements (X_{ijk}). The variance of the data modeled by Equation (10) is

$$Var(X_{ijk}) = \left[\beta_j C_k^{\gamma_j} \right]^2 Var(L_i \cdot \varepsilon_{ijk}) \quad , \qquad (12)$$

which is an increasing function of C_k. (See Reference [4] for a complete discussion of this model.)

The accuracy and precision of Method 612-Chlorinated Hydrocarbons depend upon water type through Equations (11) and (12) and the parameters (β_j) and (γ_j). If the (βj) and (γj) vary with j (i.e. vary across water type), then the accuracy and precision of the method also vary across water type.

In order to determine if these parameters do vary across water type and to compare their values, they must be estimated from the laboratory data using regression techniques. Equation (10) represents the basic model. However, taking natural logarithms of both sides of Equation (10), the following straight line regression model is obtained,

$$\ell n\, X_{ijk} = \ell n\, \beta_j + \gamma_j\, \ell n\, C_k + \ell n\, L_i + \ell n\, \varepsilon_{ijk} \quad . \qquad (13)$$

which can be analyzed using standard linear model analysis techniques. The parameter $\ell n\ \beta_j$ is the intercept and γ_j the slope of the regression line associated with water type j. It is assumed that $\ell n\ L_i$ is normally distributed with mean 0 and variance σ_L^2, and that $\ell n\ \varepsilon_{ijk}$ is normally distributed with mean 0 and variance σ_ε^2, and that the $(\ell n\ L_i)$ and $(\ell n\ \varepsilon_{ijk})$ terms are independent.

Based on Equation (13) the comparison of water types reduces to the comparison of straight lines. Distilled water is viewed as a control, and each of the remaining lines is compared directly to the line for distilled water.

Using the data on the log-log scale and regression techniques, the parameters $\ell n\ \beta_j$ (and hence β_j) and γ_j can be estimated. The estimates are then used to test the null hypothesis that there is no effect due to water type. The formal null and alternative statistical hypotheses H_0 and H_A are given by

$$H_0: \ell n\ \beta_j - \ell n\ \beta_1 = 0 \text{ and } \gamma_j - \gamma_1 = 0 \text{ for } j = 2,3,4,5,6$$

versus

$$H_A: \ell n\ \beta_j - \ell n\ \beta_1 \neq 0 \text{ and/or } \gamma_j - \gamma_1 \neq 0 \text{ for some } j = 2,3,4,5,6 \ .$$

The test of null hypothesis H_0 against the alternative hypothesis H_A is based on an F-statistic derived from standard linear model theory. The probability of obtaining a value of an F-statistic as large as the value which was actually observed (F OBS), denoted by P(F > F OBS), is calculated under the assumption that H_0 is true. The null hypothesis H_0 is rejected in favor of H_A if P(F > F OBS) is less than 0.05.

If H_0 is rejected, then some linear combination of the differences $\ell n\ \beta_j - \ell n\ \beta_1$ and $\gamma_j - \gamma_1$ is statistically different from zero. However, this does not guarantee there will be a statistically significant direct effect attributable to any specific water type since the overall F test can be overly sensitive to minor systematic effect common to several water types. The effect due to a specific water type is judged to be statistically significant only if one of the differences $\ell n\ \beta_j - \ell n\ \beta_1$ and/or $\gamma_j - \gamma_1$ is statistically different from zero. This is determined by checking the simultaneous 95% confidence intervals which are constructed for each of these differences. Each true difference can be stated to lie within its respective confidence interval with 95% confidence. If zero is contained within the confidence interval, then there is no evidence that the corresponding difference is significantly different from zero.

If at least one of the confidence intervals for the differences $\ell n\ \beta_j - \ell n\ \beta_1$ or $\gamma_j - \gamma_1$ fails to include zero, then the statistical significance of the effect due to water types has been established. However, establishment of a statistically significant effect due to water type does not necessarily mean that the effect is of practical importance. Practical importance is related to the size and interpretation of the difference.

The interpretation of the differences involves comparing the mean recovery and standard deviation of the (X_{ijk}) data for each water type to the

mean recovery and standard deviation obtained for distilled water. These comparisons are made on a relative basis. The mean recovery for water type j is given by Equation (11). The mean recovery for water type j is compared to that for distilled water (j=1) on a relative basis by

$$\frac{E(X_{ijk})}{E(X_{i1k})} = \frac{\beta_j C_k^{\gamma_j} E(L_i \cdot \varepsilon_{ijk})}{\beta_1 C_k^{\gamma_1} E(L_i \cdot \varepsilon_{i1k})} = \frac{\beta_j}{\beta_1} C_k^{\gamma_j - \gamma_1} \quad . \qquad (14)$$

(The ratio of the standard deviations would be equivalent to Equation (14) and therefore the interpretation of the effect on precision is the same as that for the effect on mean recovery.)

The ratio in Equation (14) is a measure of the relative difference in mean recovery between water type j and distilled water. It is composed of two parts (a) β_j/β_1, which is independent of the true concentration level (i.e. the constant bias), and (b) $C_k^{\gamma_j - \gamma_1}$ which depends upon the true concentration level (i.e. the concentration dependent bias). If $\gamma_j - \gamma_1$ is zero, then the relative difference in mean recovery is just β_j/β_1 which is independent of concentration level C_k. Therefore, it can then be stated that the mean recovery of water type j is (β_j/β_1) X 100% of the mean recovery for distilled water. If $\gamma_j - \gamma_1$ is not zero, then the mean recovery of water type j is (β_j/β_1). $(C_k^{\gamma_j - \gamma_1})$ X 100% of that for distilled water, and therefore depends upon the true concentration level C_k.

In order to illustrate these points consider the following example. Suppose that a significant F-value has been obtained, and the confidence intervals for all the differences contain zero except for water type 5. For water type 5, the point estimate for $\ln \beta_5 - \ln \beta_1$ is 0.38 and the confidence interval for $\ln \beta_5 - \ln \beta_1$ is (-0.69, -0.07). The point estimate for $\gamma_5 - \gamma_1$ is 0.07, and the confidence interval for $\gamma_5 - \gamma_1$ is (-0.04, 0.18). In this case a statistically significant effect due to water type has been established which involves only water type 5. The practical significance of this effect is judged by considering Equation (14). The ratio of mean recoveries for water type 5 and distilled water is given by

$$\frac{E(X_{ik})}{E(X_{i1k})} = \frac{\beta_5}{\beta_1} C_k^{\gamma_5 - \gamma_1} \quad , \qquad (15)$$

and the ratio of the standard deviations is given by

$$\sqrt{\frac{Var(X_{ijk})}{Var(X_{i1k})}} = \frac{\beta_5}{\beta_1} C_k^{\gamma_5 - \gamma_1} \qquad (16)$$

Since the confidence interval for $\gamma_5 - \gamma_1$ contains zero, this difference is assumed to be insignificant and is set to zero. Therefore Equations (15) and (16) reduce to β_5/β_1. The point estimate for $\ln \beta_5 - \ln \beta_1$ was -0.38. Therefore, the point estimate for β_5/β_1 is 0.68, and the mean recovery for water type 5 is estimated to be 68% of the mean recovery

for distilled water. Similarly the standard deviation for the data for water type 5 is estimated to be 68% of the standard deviation for distilled water. Since the 95% confidence interval for $\ell n\ \beta_5 - \ell n\ \beta_1$ was (-0.69, -0.07), any value in the interval (0.50, 0.93) is a reasonable estimate for β_5/β_1, and the mean recovery (standard deviation) for water type 5 can be claimed to be from 50% to 93% of the mean recovery (standard deviation) for distilled water. The practical significance of the effect due to water type 5 would depend upon the importance of a mean recovery (standard deviation) which is between 50% and 93% of the mean recovery (standard deviation) observed for distilled water.

The comparison of accuracy and precision across water types just discussed is based on the assumption that Equation (10) approximately models the data. It is clear that in practical monitoring programs of this type such models cannot model the data completely in every case. This analysis therefore is viewed as a screening procedure which identifies those cases where differences in water types are likely to be present. A more detailed, local analysis can then be pursued using the basic summary statistics for precision and accuracy.

SECTION 4

RESULTS AND DISCUSSION

The purpose of this study was to determine the precision and accuracy for the chlorinated hydrocarbons of concern using a large group of representative laboratories. This interlaboratory study therefore was a realistic evaluation of the method's performance. In reviewing the data developed on the determination of the eight chlorinated hydrocarbons in the various water types, the overall data statistically fall in the ranges anticipated based on IT Enviroscience's intralaboratory study of the method. However, caution must be exercised in review and interpretation of the general observations and conclusions presented in this section. The large amount of data involved in the study dictates that there are always exceptions to each conclusion in at least one concentration, compound, or water type.

STATISTICAL SUMMARIES

The basic summary statistics discussed in Section 3 were calculated for each of the eight chlorinated hydrocarbons and are summarized in Tables 5, 6, 7, 8, 9, 10, 11, and 12. The number of outliers for each data set as determined by ranking and individual outlier test ranged from one to nine, and averaged about five outliers per data set. For all data for the eight compounds, 25% was rejected. Based on the concentration and water type for the specific compounds, the greatest percentage (31%) of outliers was obtained for 1,3-dichlorobenzene and the lowest percentage of outliers (16%) for 2-chloronaphthalene.

Review and Interpretation of Data

The following general observations and conclusions may be drawn from the statistical summaries (Tables 5 through 12) and raw data tables (Tables A-5 to 28 in the appendix):

1. Of the 20 possible data points for each compound, concentration, and water type, there were an average of more than 15 acceptable data points. Based on the concentration and water type for the specific compounds, the lowest data point average (13.8) was obtained for 1,3-dichlorobenzene and the highest data point average (16.7) for 2-chloronaphthalene.

2. The mean recovery given in the statistical summaries expressed as a percentage of the true concentration ranged from 57 to 155%, with the majority of the values in the 75 to 90% range.

TABLE 5.

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STATISTICAL SUMMARY FOR HEXACHLOROETHANE ANALYSES BY WATER TYPE

	WATER 1		WATER 2		WATER 3		WATER 4		WATER 5		WATER 6	
LOW YOUDEN PAIR	1	6	1	6	1	6	1	6	1	6	1	6
NUMBER OF DATA POINTS	14	15	14	14	16	17	16	15	15	15	13	13
TRUE CONC (C) UG/L	1.02	1.18	1.02	1.18	1.02	1.18	1.02	1.18	1.02	1.18	1.02	1.18
MEAN RECOVERY (X)	0.68	0.91	0.71	0.83	0.76	1.18	0.93	0.86	0.65	0.85	0.71	0.77
ACCURACY(%REL ERROR)	-32.88	-23.14	-30.83	-29.42	-25.28	0.09	-8.54	-26.99	-36.56	-27.94	-30.95	-34.40
OVERALL STD DEV (S)	0.27	0.27	0.14	0.27	0.28	0.90	0.36	0.29	0.21	0.24	0.19	0.12
OVERALL REL STD DEV, %	39.32	30.00	20.10	32.46	36.93	76.36	38.55	33.45	32.10	27.87	26.93	15.45
SINGLE STD DEV, (SR)	0.22		0.13		0.67		0.17		0.19		0.10	
ANALYST REL DEV, %	27.52		17.27		68.44		19.30		26.02		12.99	
MEDIUM YOUDEN PAIR	2	5	2	5	2	5	2	5	2	5	2	5
NUMBER OF DATA POINTS	15	15	15	14	17	16	15	15	16	16	14	13
TRUE CONC (C) UG/L	2.56	2.96	2.56	2.96	2.56	2.96	2.56	2.96	2.56	2.96	2.56	2.96
MEAN RECOVERY (X)	1.84	2.30	1.86	2.27	2.12	2.93	2.12	2.62	1.62	2.87	2.15	2.36
ACCURACY(%REL ERROR)	-28.02	-22.39	-27.41	-23.19	-16.99	-1.03	-17.08	-11.42	-36.87	-3.16	-16.10	-20.32
OVERALL STD DEV (S)	0.76	0.75	0.63	1.03	1.17	1.59	0.44	0.77	0.79	1.65	0.68	0.61
OVERALL REL STD DEV, %	41.18	32.70	34.11	45.18	54.90	54.34	20.95	29.35	48.66	57.60	31.50	25.90
SINGLE STD DEV, (SR)	0.75		0.70		1.00		0.42		0.84		0.47	
ANALYST REL DEV, %	36.22		33.99		39.74		17.52		37.46		20.80	
HIGH YOUDEN PAIR	3	4	3	4	3	4	3	4	3	4	3	4
NUMBER OF DATA POINTS	14	15	15	16	15	17	15	16	16	17	13	14
TRUE CONC (C) UG/L	12.30	14.80	12.80	14.80	12.80	14.80	12.80	14.80	12.80	14.80	12.80	14.80
MEAN RECOVERY (X)	8.97	10.96	10.28	10.88	9.63	11.87	10.55	11.03	8.45	9.80	10.12	11.21
ACCURACY(%REL ERROR)	-29.91	-25.96	-19.68	-26.51	-24.78	-19.79	-17.61	-25.46	-34.02	-33.79	-20.97	-24.24
OVERALL STD DEV (S)	3.09	4.27	2.54	3.19	3.80	4.37	2.26	4.10	3.09	3.51	2.05	3.26
OVERALL REL STD DEV, %	34.46	39.00	24.73	29.36	39.49	36.79	21.46	37.21	36.82	35.87	20.30	29.08
SINGLE STD DEV, (SR)	1.64		2.91		2.10		2.81		1.57		1.88	
ANALYST REL DEV, %	16.50		27.47		19.53		26.03		17.26		17.63	

WATER LEGEND

1 - DISTILLED WATER
2 - TAP WATER
3 - SURFACE WATER
4 - WASTE WATER 1
5 - WASTE WATER 2
6 - WASTE WATER 3

TABLE 6.

ENVIRONMENTAL MONITORING AND SUPPORT LABORATORY
OFFICE OF RESEARCH AND DEVELOPMENT
ENVIRONMENTAL PROTECTION AGENCY

EPA METHOD VALIDATION STUDY-IT ENVIROSCI CHLORCARS

STATISTICAL SUMMARY FOR HEXACHLOROBUTADIENE ANALYSES BY WATER TYPE

	WATER 1		WATER 2		WATER 3		WATER 4		WATER 5		WATER 6	
LOW YOUDEN PAIR	1	6	1	6	1	6	1	6	1	6	1	6
NUMBER OF DATA POINTS	15	16	14	15	13	14	15	15	13	13	16	15
TRUE CONC (C) UG/L	3.12	3.68	3.12	3.68	3.12	3.68	3.12	3.68	3.12	3.68	3.12	3.68
MEAN RECOVERY (X)	1.79	2.49	2.03	2.74	2.04	2.45	2.16	2.48	2.43	2.55	2.81	2.56
ACCURACY(%REL ERROR)	-42.50	-32.20	-34.94	-25.53	-34.49	-33.45	-30.85	-32.62	-22.09	-30.62	-9.90	-30.42
OVERALL STD DEV (S)	0.91	1.04	0.94	1.37	0.56	1.19	0.58	1.28	1.80	0.85	1.11	0.83
OVERALL REL STD DEV, %	50.94	41.88	46.48	49.82	27.63	48.60	26.68	51.43	74.23	33.21	39.39	32.55
SINGLE STD DEV, (SR)	0.47		0.45		0.73		0.79		1.05		0.61	
ANALYST REL DEV, %	21.73		18.70		32.55		34.11		42.30		22.59	
MEDIUM YOUDEN PAIR	2	5	2	5	2	5	2	5	2	5	2	5
NUMBER OF DATA POINTS	16	16	14	15	13	14	14	15	14	14	16	16
TRUE CONC (C) UG/L	23.40	27.60	23.40	27.60	23.40	27.60	23.40	27.60	23.40	27.60	23.40	27.60
MEAN RECOVERY (X)	13.89	17.88	14.89	18.97	13.82	19.28	15.39	18.39	14.00	20.43	15.72	22.18
ACCURACY(%REL ERROR)	-40.63	-35.22	-36.39	-31.28	-40.94	-30.14	-34.22	-33.38	-40.19	-25.98	-32.83	-19.65
OVERALL STD DEV (S)	6.52	9.32	6.42	9.84	3.90	6.86	3.98	7.63	8.14	7.17	6.35	6.92
OVERALL REL STD DEV, %	46.95	52.13	43.15	51.88	28.19	35.60	25.84	41.51	58.19	35.10	40.43	31.21
SINGLE STD DEV, (SR)	4.10		6.59		5.17		4.23		6.21		4.14	
ANALYST REL DEV, %	25.82		38.94		31.23		25.05		36.07		21.86	
HIGH YOUDEN PAIR	3	4	3	4	3	4	3	4	3	4	3	4
NUMBER OF DATA POINTS	16	16	15	15	13	14	15	15	14	14	16	16
TRUE CONC (C) UG/L	32.20	36.80	32.20	36.80	32.20	36.80	32.20	36.80	32.20	36.80	32.20	36.80
MEAN RECOVERY (X)	19.44	21.95	19.38	23.86	18.46	23.82	22.42	23.32	19.70	22.50	21.67	28.33
ACCURACY(%REL ERROR)	-39.64	-40.34	-39.80	-35.17	-42.67	-35.26	-30.39	-36.62	-38.82	-38.87	-32.69	-23.02
OVERALL STD DEV (S)	11.09	11.87	6.97	9.09	9.87	8.78	7.19	10.94	8.42	7.09	9.62	10.15
OVERALL REL STD DEV, %	57.08	54.09	35.96	38.11	53.48	36.84	32.05	46.91	42.72	31.53	44.39	35.82
SINGLE STD DEV, (SR)	2.38		3.53		6.36		6.12		3.89		3.66	
ANALYST REL DEV, %	11.52		16.32		30.06		26.74		18.42		14.65	

WATER LEGEND

1 - DISTILLED WATER
2 - TAP WATER
3 - SURFACE WATER
4 - WASTE WATER 1
5 - WASTE WATER 2
6 - WASTE WATER 3

TABLE 7.

ENVIRONMENTAL MONITORING AND SUPPORT LABORATORY
OFFICE OF RESEARCH AND DEVELOPMENT
ENVIRONMENTAL PROTECTION AGENCY

EPA METHOD VALIDATION STUDY-11 ENVIROSCI CHLORCARS

STATISTICAL SUMMARY FOR 2-CHLORONAPHTHALENE ANALYSES BY WATER TYPE

	WATER 1		WATER 2		WATER 3		WATER 4		WATER 5		WATER 6	
LOW YOUDEN PAIR	1	6	1	6	1	6	1	6	1	6	1	6
NUMBER OF DATA POINTS	16	17	15	15	16	15	19	17	15	16	18	16
TRUE CONC (C) UG/L	21.40	19.10	21.40	19.10	21.40	19.10	21.40	19.10	21.40	19.10	21.40	19.10
MEAN RECOVERY (X)	17.27	19.05	19.56	17.36	20.15	18.33	21.77	30.44	17.90	25.52	17.46	17.38
ACCURACY(%REL ERROR)	-19.29	-0.24	-8.60	-9.10	-5.83	-4.02	1.73	59.35	-16.34	33.60	-18.43	-9.02
OVERALL STD DEV (S)	4.27	6.98	5.44	3.03	5.10	4.22	9.22	23.81	5.70	14.10	7.52	7.20
OVERALL REL STD DEV, %	24.74	36.66	27.80	17.42	25.30	23.00	42.33	78.22	31.85	55.27	43.07	41.43
SINGLE STD DEV, (SR)	3.88		3.14		3.30		17.89		11.00		5.41	
ANALYST REL DEV, %	21.35		17.00		17.17		68.52		50.65		31.09	
MEDIUM YOUDEN PAIR	2	5	2	5	2	5	2	5	2	5	2	5
NUMBER OF DATA POINTS	18	18	16	16	16	15	17	17	17	17	18	18
TRUE CONC (C) UG/L	161.00	143.00	161.00	143.00	161.00	143.00	161.00	143.00	161.00	143.00	161.00	143.00
MEAN RECOVERY (X)	128.04	114.21	124.16	110.43	123.55	117.63	138.80	116.18	115.57	125.40	119.91	109.83
ACCURACY(%REL ERROR)	-20.47	-20.14	-22.98	-22.77	-23.26	-17.74	-13.79	-18.76	-28.22	-12.31	-25.52	-23.20
OVERALL STD DEV (S)	42.15	38.04	33.49	35.26	23.19	23.36	22.29	45.74	29.38	38.55	33.80	29.51
OVERALL REL STD DEV, %	32.92	33.30	26.97	31.93	18.77	19.86	16.06	39.37	25.43	30.75	28.19	26.87
SINGLE STD DEV, (SR)	32.82		28.13		20.23		32.26		27.60		18.15	
ANALYST REL DEV, %	27.10		23.98		16.77		25.31		22.91		15.80	
HIGH YOUDEN PAIR	3	4	3	4	3	4	3	4	3	4	3	4
NUMBER OF DATA POINTS	18	19	15	16	15	16	18	19	17	15	18	18
TRUE CONC (C) UG/L	268.00	238.00	268.00	238.00	268.00	238.00	268.00	238.00	268.00	238.00	268.00	238.00
MEAN RECOVERY (X)	202.92	173.90	199.30	179.31	204.45	191.04	226.46	175.78	193.51	184.01	196.39	182.94
ACCURACY(%REL ERROR)	-24.28	-26.93	-25.63	-24.66	-23.71	-19.73	-15.50	-26.14	-27.79	-22.68	-26.53	-23.14
OVERALL STD DEV (S)	56.43	92.44	37.92	46.11	39.19	31.97	37.86	62.81	63.11	37.87	60.58	48.14
OVERALL REL STD DEV, %	27.81	53.16	19.03	25.71	19.17	16.74	16.72	35.73	32.61	20.58	30.77	26.31
SINGLE STD DEV, (SR)	50.77		17.42		19.58		36.03		23.54		31.72	
ANALYST REL DEV, %	26.95		9.20		9.90		17.92		12.47		16.70	

WATER LEGEND

1 - DISTILLED WATER
2 - TAP WATER
3 - SURFACE WATER
4 - WASTE WATER 1
5 - WASTE WATER 2
6 - WASTE WATER 3

TABLE 8.

ENVIRONMENTAL MONITORING AND SUPPORT LABORATORY
OFFICE OF RESEARCH AND DEVELOPMENT
ENVIRONMENTAL PROTECTION AGENCY

EPA METHOD VALIDATION STUDY 11 ENVIROSCI CHLDRCARS

STATISTICAL SUMMARY FOR 1,2-DICHLOROBENZENE ANALYSES BY WATER TYPE

	WATER 1		WATER 2		WATER 3		WATER 4		WATER 5		WATER 6	
LOW YOUDEN PAIR	1	6	1	6	1	6	1	6	1	6	1	6
NUMBER OF DATA POINTS	15	15	16	16	14	12	16	16	13	13	14	16
TRUE CONC (C) UG/L	29.80	35.60	29.80	35.60	29.80	35.60	29.80	35.60	29.80	35.60	29.80	35.60
MEAN RECOVERY (X)	23.04	31.77	29.17	42.63	25.52	28.31	24.35	30.33	26.22	36.11	28.69	40.25
ACCURACY(%REL ERROR)	-22.68	-10.75	-2.12	19.74	-14.38	-20.48	-18.27	-14.82	-12.03	1.42	-3.71	13.05
OVERALL STD DEV (S)	6.60	7.19	12.27	23.45	5.81	6.77	10.23	12.79	8.54	12.06	7.70	18.40
OVERALL REL STD DEV, %	28.66	22.62	42.05	55.02	22.77	23.92	42.01	42.18	32.56	33.40	26.82	45.72
SINGLE STD DEV, (SR)	3.29		16.76		3.89		8.26		8.27		10.13	
ANALYST REL DEV, %	12.00		46.69		14.46		30.20		26.53		29.39	
MEDIUM YOUDEN PAIR	2	5	2	5	2	5	2	5	2	5	2	5
NUMBER OF DATA POINTS	17	17	16	16	14	14	16	16	15	15	16	16
TRUE CONC (C) UG/L	149.00	178.00	149.00	178.00	149.00	178.00	149.00	178.00	149.00	178.00	149.00	178.00
MEAN RECOVERY (X)	133.14	154.11	142.78	169.15	111.53	145.76	127.04	154.38	115.27	168.48	131.22	166.74
ACCURACY(%REL ERROR)	-10.64	-13.42	-4.19	-4.97	-25.15	-18.11	-14.73	-13.27	-22.64	-5.35	-11.93	-6.33
OVERALL STD DEV (S)	48.79	49.85	51.56	67.45	37.26	41.01	30.43	44.56	28.29	58.02	33.34	51.71
OVERALL REL STD DEV, %	36.65	32.34	36.12	39.88	33.41	28.13	23.95	28.86	24.54	34.44	25.41	31.01
SINGLE STD DEV, (SR)	25.37		51.71		41.34		26.53		36.32		25.10	
ANALYST REL DEV, %	17.66		33.15		32.13		18.88		25.60		16.85	
HIGH YOUDEN PAIR	3	4	3	4	3	4	3	4	3	4	3	4
NUMBER OF DATA POINTS	17	17	14	16	14	14	16	16	15	15	16	16
TRUE CONC (C) UG/L	298.00	356.00	298.00	356.00	298.00	356.00	298.00	356.00	298.00	356.00	298.00	356.00
MEAN RECOVERY (X)	234.89	300.51	253.05	300.26	241.68	309.83	256.96	288.45	239.71	303.63	251.49	316.09
ACCURACY(%REL ERROR)	-21.18	-15.59	-15.08	-15.66	-18.90	-12.97	-13.77	-18.97	-19.56	-14.71	-15.61	-11.21
OVERALL STD DEV (S)	100.23	134.90	66.87	91.24	93.79	68.87	75.89	83.72	103.41	98.77	90.24	97.40
OVERALL REL STD DEV, %	42.67	44.89	26.43	30.39	38.81	22.23	29.53	29.02	43.14	32.53	35.88	30.81
SINGLE STD DEV, (SR)	63.86		36.90		65.95		32.80		53.97		75.25	
ANALYST REL DEV, %	23.85		13.34		23.92		12.03		19.87		26.52	

WATER LEGEND

1 - DISTILLED WATER
2 - TAP WATER
3 - SURFACE WATER
4 - WASTE WATER 1
5 - WASTE WATER 2
6 - WASTE WATER 3

TABLE 9.

ENVIRONMENTAL MONITORING AND SUPPORT LABORATORY
OFFICE OF RESEARCH AND DEVELOPMENT
ENVIRONMENTAL PROTECTION AGENCY

EPA METHOD VALIDATION STUDY-11 ENVIROSCI CHLORCARB

STATISTICAL SUMMARY FOR 1,3-DICHLOROBENZENE ANALYSES BY WATER TYPE

	WATER 1		WATER 2		WATER 3		WATER 4		WATER 5		WATER 6	
LOW YOUDEN PAIR	1	6	1	6	1	6	1	6	1	6	1	6
NUMBER OF DATA POINTS	14	12	14	14	12	12	13	12	12	14	14	14
TRUE CONC (C) UG/L	20.40	23.80	20.40	23.80	20.40	23.80	20.40	23.80	20.40	23.80	20.40	23.80
MEAN RECOVERY (X)	14.77	19.24	19.91	21.91	16.18	18.25	21.20	21.99	15.59	19.48	18.28	18.46
ACCURACY(%REL ERROR)	-27.59	-19.15	-2.40	-7.92	-20.69	-23.32	3.94	-7.60	-23.57	-18.17	-10.39	-22.45
OVERALL STD DEV (S)	4.44	2.88	9.52	9.41	3.72	3.16	7.38	6.08	5.02	8.30	5.87	6.29
OVERALL REL STD DEV, %	30.06	14.97	47.83	42.94	23.01	17.33	34.80	27.64	32.18	42.62	32.10	34.06
SINGLE STD DEV, (SR)	2.37		7.07		2.83		2.97		5.74		3.48	
ANALYST REL DEV, %	13.94		33.83		16.45		13.77		32.75		18.95	
MEDIUM YOUDEN PAIR	2	5	2	5	2	5	2	5	2	5	2	5
NUMBER OF DATA POINTS	15	15	15	14	13	12	13	13	15	15	14	14
TRUE CONC (C) UG/L	51.00	59.40	51.00	59.40	51.00	59.40	51.00	59.40	51.00	59.40	51.00	59.40
MEAN RECOVERY (X)	37.82	40.88	54.47	47.39	36.57	43.79	45.39	46.72	40.88	53.59	36.79	39.81
ACCURACY(%REL ERROR)	-25.84	-31.18	6.81	-20.21	-28.30	-26.28	-11.01	-21.35	-19.85	-9.77	-27.86	-32.98
OVERALL STD DEV (S)	18.62	14.16	31.17	17.71	11.27	4.63	19.27	17.19	21.52	25.88	10.18	11.66
OVERALL REL STD DEV, %	49.23	34.65	57.23	37.36	30.81	10.58	42.46	36.81	52.65	47.92	27.66	29.30
SINGLE STD DEV, (SR)	8.34		19.69		5.85		7.67		12.57		5.93	
ANALYST REL DEV, %	21.18		38.67		14.55		16.66		26.61		15.49	
HIGH YOUDEN PAIR	3	4	3	4	3	4	3	4	3	4	3	4
NUMBER OF DATA POINTS	15	15	14	15	13	13	15	15	14	15	15	15
TRUE CONC (C) UG/L	204.00	238.00	204.00	238.00	204.00	238.00	204.00	238.00	204.00	238.00	204.00	238.00
MEAN RECOVERY (X)	150.62	172.29	163.96	176.70	153.92	185.91	163.96	196.70	138.38	172.64	151.06	186.24
ACCURACY(%REL ERROR)	-26.17	-27.61	-19.63	-25.76	-24.55	-21.89	-19.63	-17.35	-32.16	-27.46	-25.95	-21.75
OVERALL STD DEV (S)	72.07	77.73	39.54	67.65	55.31	36.61	45.05	63.94	43.26	51.86	51.70	63.90
OVERALL REL STD DEV, %	47.85	45.11	24.12	38.29	35.93	19.69	27.48	32.51	31.26	30.04	34.22	34.31
SINGLE STD DEV, (SR)	30.02		31.07		30.22		27.84		28.79		27.56	
ANALYST REL DEV, %	18.60		18.24		17.78		15.44		18.51		18.34	

WATER LEGEND

1 - DISTILLED WATER
2 - TAP WATER
3 - SURFACE WATER
4 - WASTE WATER 1
5 - WASTE WATER 2
6 - WASTE WATER 3

TABLE 10.

ENVIRONMENTAL MONITORING AND SUPPORT LABORATORY
OFFICE OF RESEARCH AND DEVELOPMENT
ENVIRONMENTAL PROTECTION AGENCY

EPA METHOD VALIDATION STUDY-IT ENVIROSCI CHLORCARS

STATISTICAL SUMMARY FOR 1,4-DICHLOROBENZENE ANALYSES BY WATER TYPE

	WATER 1		WATER 2		WATER 3		WATER 4		WATER 5		WATER 6	
LOW YOUDEN PAIR	1	6	1	6	1	6	1	6	1	6	1	6
NUMBER OF DATA POINTS	14	17	15	14	17	17	14	15	14	14	14	13
TRUE CONC (C) UG/L	23.00	26.00	23.00	26.00	23.00	26.00	23.00	26.00	23.00	26.00	23.00	26.00
MEAN RECOVERY (X)	17.79	23.44	20.74	24.22	21.20	25.76	21.12	20.58	19.59	23.43	20.13	21.18
ACCURACY(%REL ERROR)	-22.63	-9.85	-9.83	-6.84	-7.84	-0.92	-8.16	-20.85	-14.84	-9.69	-12.48	-18.55
OVERALL STD DEV (S)	5.86	7.51	11.33	11.87	9.24	10.92	8.58	10.58	8.95	8.87	3.69	3.04
OVERALL REL STD DEV, %	32.91	32.04	54.62	49.62	43.59	42.40	40.59	51.41	45.69	37.85	18.34	14.36
SINGLE STD DEV, (SR)	2.93		7.06		9.18		4.08		5.08		2.92	
ANALYST REL DEV, %	14.20		31.42		39.08		19.58		23.62		14.13	
MEDIUM YOUDEN PAIR	2	5	2	5	2	5	2	5	2	5	2	5
NUMBER OF DATA POINTS	16	17	15	15	17	17	16	16	16	16	16	16
TRUE CONC (C) UG/L	172.00	194.00	172.00	194.00	172.00	194.00	172.00	194.00	172.00	194.00	172.00	194.00
MEAN RECOVERY (X)	132.29	144.16	136.61	155.48	129.26	148.88	137.47	146.10	133.83	165.19	132.36	155.47
ACCURACY(%REL ERROR)	-23.09	-25.69	-20.57	-19.85	-24.85	-22.26	-20.07	-24.69	-22.19	-14.85	-23.05	-19.86
OVERALL STD DEV (S)	27.89	44.47	48.66	48.94	61.02	52.20	43.78	35.34	46.36	57.25	44.36	33.13
OVERALL REL STD DEV, %	21.08	30.84	35.62	31.47	47.21	35.06	31.85	24.19	34.64	34.66	33.52	21.31
SINGLE STD DEV, (SR)	20.10		47.02		29.94		42.49		33.96		31.05	
ANALYST REL DEV, %	14.54		32.19		21.53		29.97		22.71		21.58	
HIGH YOUDEN PAIR	3	4	3	4	3	4	3	4	3	4	3	4
NUMBER OF DATA POINTS	17	17	14	15	17	17	16	16	16	16	16	16
TRUE CONC (C) UG/L	288.00	324.00	288.00	324.00	288.00	324.00	288.00	324.00	288.00	324.00	288.00	324.00
MEAN RECOVERY (X)	203.35	227.42	207.79	240.31	212.74	238.21	237.39	247.55	228.42	241.99	221.53	258.28
ACCURACY(%REL ERROR)	-29.39	-29.81	-27.85	-25.83	-26.13	-26.48	-17.57	-23.59	-20.69	-25.31	-23.08	-20.26
OVERALL STD DEV (S)	88.80	95.11	57.10	54.49	102.61	92.08	65.89	68.50	87.35	76.44	84.92	85.83
OVERALL REL STD DEV, %	43.67	41.82	27.48	22.68	48.23	38.65	27.76	27.67	38.24	31.59	38.34	33.23
SINGLE STD DEV, (SR)	38.05		24.21		42.95		42.22		37.69		55.69	
ANALYST REL DEV, %	17.87		10.80		19.05		17.41		16.02		23.21	

WATER LEGEND

1 - DISTILLED WATER
2 - TAP WATER
3 - SURFACE WATER
4 - WASTE WATER 1
5 - WASTE WATER 2
6 - WASTE WATER 3

TABLE 11.

ENVIRONMENTAL MONITORING AND SUPPORT LABORATORY
OFFICE OF RESEARCH AND DEVELOPMENT
ENVIRONMENTAL PROTECTION AGENCY

EPA METHOD VALIDATION STUDY-11 ENVIROSCI CHLORCARS

STATISTICAL SUMMARY FOR 1,2,4 TRICHLOROBENZENE ANALYSES BY WATER TYPE

	WATER 1		WATER 2		WATER 3		WATER 4		WATER 5		WATER 6	
LOW YOUDEN PAIR	1	6	1	6	1	6	1	6	1	6	1	6
NUMBER OF DATA POINTS	15	14	15	15	16	14	15	15	13	13	13	14
TRUE CONC (C) UG/L	15.10	17.30	15.10	17.30	15.10	17.30	15.10	17.30	15.10	17.30	15.10	17.30
MEAN RECOVERY (X)	12.13	14.35	11.42	14.82	12.51	15.10	12.11	12.72	10.91	14.12	14.48	14.17
ACCURACY(%REL ERROR)	-19.66	-17.03	-24.38	-15.51	-17.14	-12.73	-19.82	-26.50	-27.74	-18.37	-4.08	-18.11
OVERALL STD DEV (S)	3.70	2.46	3.70	5.23	5.88	7.01	3.63	4.78	4.22	3.52	4.42	3.99
OVERALL REL STD DEV, %	30.53	24.08	32.42	35.80	45.38	46.43	29.99	37.61	38.76	24.94	30.54	28.17
SINGLE STD DEV, (SR)	2.25		1.98		2.82		2.83		1.92		3.15	
ANALYST REL DEV, %	18.98		15.19		20.44		22.77		15.37		22.02	
MEDIUM YOUDEN PAIR	2	5	2	5	2	5	2	5	2	5	2	5
NUMBER OF DATA POINTS	15	15	15	15	16	14	15	16	13	13	14	14
TRUE CONC (C) UG/L	37.80	43.20	37.80	43.20	37.80	43.20	37.80	43.20	37.80	43.20	37.80	43.20
MEAN RECOVERY (X)	29.84	37.02	28.09	31.53	38.33	38.28	28.04	40.70	28.28	43.71	31.71	39.96
ACCURACY(%REL ERROR)	-21.05	-14.32	-25.70	-27.00	3.89	-11.28	-25.81	-5.79	-25.18	1.17	-16.11	-7.51
OVERALL STD DEV (S)	12.57	13.76	10.56	12.19	19.99	13.19	10.58	17.73	8.77	17.02	7.01	17.86
OVERALL REL STD DEV, %	42.11	37.18	38.88	38.66	55.01	34.48	37.73	43.57	31.02	38.94	22.12	44.70
SINGLE STD DEV, (SR)	10.34		8.55		7.80		11.25		13.31		10.70	
ANALYST REL DEV, %	30.92		28.67		20.97		32.73		36.98		29.86	
HIGH YOUDEN PAIR	3	4	3	4	3	4	3	4	3	4	3	4
NUMBER OF DATA POINTS	15	16	13	15	14	15	16	16	14	14	14	14
TRUE CONC (C) UG/L	188.00	216.00	188.00	216.00	188.00	216.00	188.00	216.00	188.00	216.00	188.00	216.00
MEAN RECOVERY (X)	132.53	109.58	133.88	139.05	128.97	142.90	138.90	144.88	140.29	159.52	146.55	159.78
ACCURACY(%REL ERROR)	-29.51	-21.49	-28.79	-35.63	-31.40	-33.84	-26.12	-32.93	-25.38	-26.15	-22.05	-26.03
OVERALL STD DEV (S)	35.80	77.20	26.01	47.89	57.88	59.73	50.06	64.89	42.82	44.64	43.84	55.29
OVERALL REL STD DEV, %	27.02	45.52	19.43	34.44	44.88	41.10	36.04	44.79	30.52	27.98	29.92	34.60
SINGLE STD DEV, (SR)	25.81		11.08		19.50		52.97		23.39		13.71	
ANALYST REL DEV, %	17.09		8.12		14.34		37.33		15.61		8.95	

WATER LEGEND

1 - DISTILLED WATER
2 - TAP WATER
3 - SURFACE WATER
4 - WASTE WATER 1
5 - WASTE WATER 2
6 - WASTE WATER 3

TABLE 12.

ENVIRONMENTAL MONITORING AND SUPPORT LABORATORY
OFFICE OF RESEARCH AND DEVELOPMENT
ENVIRONMENTAL PROTECTION AGENCY

EPA METHOD VALIDATION STUDY 11 ENVIROSCI CHLORCARS

STATISTICAL SUMMARY FOR HEXACHLOROBENZENE ANALYSES BY WATER TYPE

	WATER 1		WATER 2		WATER 3		WATER 4		WATER 5		WATER 6	
LOW YOUDEN PAIR	1	6	1	6	1	6	1	6	1	6	1	6
NUMBER OF DATA POINTS	15	14	16	16	15	15	14	15	14	16	15	15
TRUE CONC (C) UG/L	1.49	1.29	1.49	1.29	1.49	1.29	1.49	1.29	1.49	1.29	1.49	1.29
MEAN RECOVERY (X)	1.23	1.12	1.28	1.12	1.44	1.16	1.31	1.40	1.45	1.44	1.09	1.30
ACCURACY(%REL ERROR)	-17.53	-12.82	-14.38	-12.98	-3.58	-10.40	-12.24	8.32	-2.44	11.49	-26.71	0.55
OVERALL STD DEV (S)	0.28	0.21	0.28	0.19	0.42	0.19	0.28	0.54	0.75	0.67	0.45	0.52
OVERALL REL STD DEV, %	22.95	18.48	22.20	17.01	29.06	16.72	21.18	38.92	51.60	46.68	40.95	40.26
SINGLE STD DEV, (SR)	0.23		0.17		0.23		0.34		0.19		0.24	
ANALYST REL DEV, %	19.80		13.81		17.87		25.16		13.24		19.94	
MEDIUM YOUDEN PAIR	2	5	2	5	2	5	2	5	2	5	2	5
NUMBER OF DATA POINTS	15	15	16	16	14	13	16	15	14	16	15	16
TRUE CONC (C) UG/L	7.44	6.46	7.44	6.46	7.44	6.46	7.44	6.46	7.44	6.46	7.44	6.46
MEAN RECOVERY (X)	6.10	6.08	5.60	6.35	6.28	6.45	6.03	6.15	6.39	7.25	6.06	5.58
ACCURACY(%REL ERROR)	-18.04	-6.13	-24.70	-1.67	-15.57	-0.19	-18.98	-4.73	-14.15	12.31	-18.60	-13.56
OVERALL STD DEV (S)	1.82	1.70	2.07	1.61	1.08	1.16	1.50	1.06	2.61	3.73	1.98	2.75
OVERALL REL STD DEV, %	29.90	28.06	37.01	25.37	17.27	17.99	24.91	17.18	40.88	51.36	32.67	49.30
SINGLE STD DEV, (SR)	1.13		1.83		0.69		0.92		1.38		1.37	
ANALYST REL DEV, %	18.64		30.56		10.36		15.06		19.88		23.54	
HIGH YOUDEN PAIR	3	4	3	4	3	4	3	4	3	4	3	4
NUMBER OF DATA POINTS	15	15	14	16	14	14	15	16	16	14	15	15
TRUE CONC (C) UG/L	14.90	12.90	14.90	12.90	14.90	12.90	14.90	12.90	14.90	12.90	14.90	12.90
MEAN RECOVERY (X)	12.75	11.11	13.34	12.93	14.76	12.85	13.31	11.54	16.23	12.01	11.82	11.54
ACCURACY(%REL ERROR)	-14.42	-13.87	-10.45	0.26	-0.91	-0.41	-10.67	-10.52	8.90	-6.93	-20.67	-10.55
OVERALL STD DEV (S)	4.22	4.78	2.83	4.68	4.19	2.84	2.57	2.06	8.71	1.88	4.61	3.92
OVERALL REL STD DEV, %	33.06	43.00	21.22	36.19	28.40	22.08	19.32	17.83	53.69	15.64	39.01	33.93
SINGLE STD DEV, (SR)	1.37		1.62		1.13		1.49		3.74		2.64	
ANALYST REL DEV, %	11.50		12.35		8.20		12.02		26.47		22.63	

WATER LEGEND

1 - DISTILLED WATER
2 - TAP WATER
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6 - WASTE WATER 3

The lowest mean recovery value was in the low Youden pair for hexachlorobutadiene in distilled water, while the highest mean recovery value was in the low Youden pair for 2-chloronapthalene in wastewater No 1.

The low value for the hexachlorobutadiene in ampul No. 1 in distilled water seems to be an unexplainable data anomaly since better recoveries were reported for the sample ampul in other water types as well as the other ampul in the pair in all water types. The high value for 2-chloronaphthalene in wastewater No. 1, ampul No. 6, reflected the fact that 12 of the 17 laboratories having acceptable results had recoveries of greater than 100% true value. These data again appear abnormal in relation to the other ampul in the pair as well as the other water types. In reviewing the raw data the results of two laboratories, No. 31 and No. 151, were 89.3 and 90.0 µg/L versus a true value of 19.1 µg/L. These data definitely influenced the high average recovery. The chromatograms and raw data calculations support the high values reported by the laboratories, but provide no insight into the reasons for the high values.

The average mean recovery of the six concentrations and six water types for each compound compared well with data generated by IT Enviroscience on distilled water and industrial effluents during development of the analytical methodology. These data are presented in Table 13. The interlaboratory study data are therefore in the predicted range.

With the exception of the low level 2-chloronaphthalene, the percent recoveries for each compound do not appear to vary within the concentration levels used in this study.

TABLE 13. COMPARISON OF % RECOVERIES OF CHLORINATED HYDROCARBONS

Compound	IT Enviroscience % Recovery*	Interlaboratory % Recovery
Hexachloroethane	70.5	77.6
Hexachlorobutadiene	66.4	66.8
2-Chloronaphthalene	91.2	85.1
1,2-Dichlorobenzene	91.0	88.0
1,3-Dichlorobenzene	82.4	80.0
1,4-Dichlorobenzene	80.5	80.5
1,2,4-Trichlorobenzene	89.4	79.2
Hexachlorobenzene	77.3	90.2

*Mean recovery expressed as percentage of true value of all concentrations and water types analyzed.

3. The precision as measured by the overall standard deviation (S) in µg/L was found to be similar between most Youden pairs and increased in numerical value with concentration as expected. There were several cases, however, where the S within Youden pairs was quite different.

The abnormality was not consistent with any water type, concentration, or compound and therefore must be related to laboratory random errors. Examples of difference for S between Youden pairs are:

Hexachloroethane - Surface Water

Youden Pair	Ampul 1	Ampul 6
S =	0.28	0.90

2-Chloronaphthalene - Distilled Water

Youden Pair	Ampul 3	Ampul 4
S =	56.4	92.4

1,3-Dichlorobenzene - Tap Water

Youden Pair	Ampul 2	Ampul 5
S =	31.2	17.7

One fact that contributes to this precision difference within Youden pairs is the fact that one pair member may have data scatter which will allow, by creating a higher standard deviation, the retention of data that would be rejected as outliers if they were part of the other pair member's data. This is best illustrated with an example, such as the hexachloroethane low Youden pair for surface water. In the ampul No. 1 results all raw data values greater than 1.28 were rejected prior to computation of the reported standard deviation of 0.28 µg/L. A total of four values were rejected. In the case of ampul No. 6 three values were rejected and six values greater than 1.28 (1.31, 1.40, 1.50, 1.50, 3.32, and 3.46) were retained for calculation of the standard deviation of 0.90 µg/L. If in fact the two higher values (3.32 and 3.46) had been rejected prior to the computation, the standard deviation for ampul No. 6 would have been 0.37 µg/L.

Based on the results as computed by this program, the accuracy expressed as percent relative error is - 25.3 for ampul No. 1 and +0.09 for ampul No. 6. If the two higher values (3.32 and 3.46) had been rejected, as explained in the previous paragraph, the percent relative error would have been - 24.9 for ampul No. 6.

The problem can also be illustrated by reviewing the range of the retained data for each ampul.

Ampul No. 1 from 0.20 to 1.28 µg/L
Ampul No. 6 from 0.39 to 3.46 µg/L

The cause of the data scatter within Youden pairs is therefore due to random error.

4. The values of the percent relative standard deviation ranged from 11% for ampul 5, 1,3-dichlorobenzene in surface water, to 78% for ampul 6, 2-chloronaphthalene, in wastewater No. 1. The majority (91%) of the values were in the 15 to 50% range. As with the standard deviation there were values showing Youden pair differences, but overall the values were consistent between concentration levels for each compound and water type.

The principal reason for the 15 to 50% relative deviation range for the majority of the values is the scatter of the results among the laboratories for a particular compound in a water type. This scatter between laboratories may be due to the differences in skill and care taken by the analysts and the equipment and facilities available to them, but is within the limits of "normal" analyses for organic compounds in water based on the experience of IT Enviroscience.

5. The single-analyst standard deviation values (SR) were better than the overall standard deviation (S) values. In other words, SR values are less than S values. This is the expected result since the calculation of the single-analyst standard deviation utilized the difference (D) in the Youden pair for each participant and D quantities contain no systematic errors, only random ones.

6. The percent single-analyst relative deviation values as anticipated are lower than the overall relative deviation. The single-analyst statistical values do show some random variation from compound to compound and by water type and concentration, but are better than the overall relative deviation. The values range from 8.1 to 68.5% with the majority of the values in the 15 to 30% range.

7. The statistical values for single-analyst standard deviation, overall standard deviation, and the mean recovery on the low Youden pairs were not significantly different from the higher pairs. The method therefore may be utilized at the concentrations of the low Youden pair values with assurance.

8. The compound showing the most disappointing results was 2-chloronaphthalene. Differences in recoveries, standard deviations, and accuracies as percent relative error were especially prominent in the wastewater samples. Selected outlying data were reviewed with individual analysts to determine whether outliers had been caused by calculation errors or mislabeling of chromatograms. This review failed to resolve the discrepancies. The compound is not frequently encountered in trace organic analysis, therefore the lack of experience in analyzing 2-chloronapthalene at trace levels may have contributed to the scatter in the results.

9. In measuring precision with the use of Youden pairs the values determined for the pair by an individual laboratory should be only slightly dissimilar. The raw data show several examples where a laboratory determined and reported quite dissimilar results for a Youden pair. Examples are:

Laboratory No. 151	High Pair Hexachloroethane Wastewater No. 2	23.2 vs 12.7 µg/L
Laboratory No. 131	Low Pair 2-Chloronaphthalene Distilled water	2.33 vs 0.69 µg/L
Laboratory No. 81	High Pair 1,3-Dichlorobenzene Surface water	0.55 vs 1.45 µg/L

This is a sign of significant random errors.

10. Of the raw data from laboratory No. 181 98% were statistically rejected as outliers because of high results. The laboratory was asked to review its data and procedures for errors in calculation or in analytcal techniques, but none were reported.

11. Most of the hexachloroethane data for all three Youden pairs in all water types for laboratories No. 41 and No. 211 were statistically rejected as outliers. The data were too high. The laboratories may have had a contamination problem, error in standard preparation, or error in calculation.

12. Most of the hexachloroethane data for all three Youden pairs in all water types for laboratories No. 21 and No. 31 were statistically rejected as outliers. The data were too low. The laboratories may have had an error in standard preparation or calculation. The sample preparation is not suspect because few data were rejected for the other compounds.

13. Most of the hexachlorobutadiene data for three Youden pairs of all water types for laboratory No. 31 were statistically rejected as outliers. The data were too low. The laboratory may have had an error in standard preparation or calculation. The sample preparation is not suspect because few data were rejected for the other compounds with the exception of hexachloroethane.

14. All of the hexachlorobutadiene data for three Youden pairs of all water types for laboratory No. 141 were statistically rejected as outliers. The data were too high by a factor of 5 to 10. The laboratory may have had a contamination problem, error in standard preparation, or error in calculation.

15. All of the data for the three dichlorobenzenes from laboratory No. 191 were low by a factor of 5 to 10. The dilution of their standards must have been incorrect or calculation of the weighed standards improperly done. Another possibility includes loss of the dichlorobenzenes during the Kuderna-Danish concentration step during sample preparation.

16. Most of the 1,2,- and 1,3-dichlorobenzene data for all three Youden pairs in all water types for laboratory No. 211 were statistically rejected as outliers. The data were too high by a factor of 2 to 5. The laboratory may have had a contamination problem, error in standard preparation, or error in calculation.

17. All of the 1,3-dichlorobenzene data for three Youden pairs of all water types for laboratory No. 81 were statistically rejected as outliers. The data were too low by a factor of 5 to 100. The laboratory may have had an error in standard preparaton or calculation. The sample preparation is not suspect due to the fact that the 1,2- and 1,4-dichlorobenzene analyses resulted in less data rejections.

18. The majority of the 1,3-dichlorobenzene data for three Youden pairs of all types for laboratory No. 91 were statistically rejected as outliers. The data were generally too high by a factor of 2 to 3. The laboratory may have had a contamination problem, or error in standard preparation.

19. The majority of the 1,2,4-trichlorobenzene data for three Youden pairs of all water types for laboratories No. 41, No. 141, and No. 211 were statistically rejected as outliers. The data were too high by a factor of 2 to 3 for laboratory No. 211 and a factor of 3 to 10 for laboratories No. 41 and No. 141. The laboratories may have had contamination problems, errors in standard preparation, or calculation errors. The sample preparation is not suspect due to the fact all three laboratories had mostly non-rejected data for the other compounds.

20. The majority of the 1,2,4-trichlorobenzene data for three Youden pairs of all water types for laboratory No. 81 were statistically rejected as outliers. The data were generally too low by a factor of 3 to 10. The laboratory may have had an error in standard preparation or calculation. The sample preparation is not suspect because of the acceptable data for all other compounds except 1,3-dichlorobenzene.

21. All of the hexachlorobenzene data for the three Youden pairs of all water types for laboratory No. 41 were statistically rejected as outliers. The data were too high by a factor of 10. The laboratory may have had a contamination problem, error in standard preparation, or error in calculation.

22. The majority of the hexachlorobenzene data for the three Youden pairs of all water types for laboratory No. 141 were statistically rejected as outliers. The data were too high by a factor of 2 to 3. The laboratory may have had a contamination problem, error in standard preparation, or an error in calculation.

23. The majority of the hexachlorobenzene data for the three Youden pairs of all water types for laboratory No. 131 were statistically rejected as outliers. The data were too low by a factor of 5 to 50. The laboratory may have had an error in standard preparation or calculation. The sample preparation could also be the problem as many of their results for all compounds were low and rejected as outliers.

PRECISION AND ACCURACY REGRESSION EQUATIONS

The linear regression equations for precision as S and SR versus mean recovery are presented in Table 2. The equations are by compound and water type. The slope of the line may be used to estimate the standard deviation data when the intercept is insignificant, i.e. <10% of the total value.

In all cases the SR single-analyst standard deviation line slope was less than the S overall standard deviation, as would be predicted. In the majority of cases the line's intercept went through or approached the origin. There are several examples, however, where the intercept was a positive value greater than one signifying a systematic error affecting the

precision. This effect can be quite a significant percentage at lower concentrations. An example of the worst case of high numerical intercepts is 2-chloronaphthalene in Wastewater No. 1 where:

$$SR = 0.12X + 14.77$$

$$S = 0.24X + 8.18$$

There were few negative intercepts greater than one but the largest were with 1,2-dichlorobenzene in distilled/deionized water and surface water. This implies significant improvement in precision as the concentration decreases. In both cases, however, the middle concentration values were low, forcing the line below the lower and high point values and giving a negative intercept.

The linear regression equations for mean recovery versus true concentration are presented in Table 2. The equations are by compound and water type. Observation of the equations shows that 100% recovery was not achieved for any of the compounds in any of the water types. The majority of the lines go through or approach the origin with intercepts of less than one. Positive or negative intercepts greater than one were quite random through the water types, but two compounds (2-chloronaphthalene and 1,4-dichlorobenzene) both had positive intercepts greater than one for all the water types. This signifies a systematic error for these compounds which would give a background level for the compound when the concentration added was zero and a false high mean recovery for low concentration recoveries. In reviewing the data on these compounds reported by the laboratories on the various water types, few, if any, laboratories reported finding any of the compounds in the blank water samples.

The intercepts are significantly high, in some cases 8 to 10 µg/L, and should have been found in the blanks if run at the same sensitivity as the low Youden pair. In reviewing the chromatograms it was learned that some laboratories did not run the blanks at the same sensitivity as the low Youden pair.

The majority of the participating laboratories detected a significant background level of hexachlorobenzene in both wastewater No. 1 and wastewater No. 3. The mean hexachlorobenzene concentration was 0.12 µg/L and 0.09 µg/L respectively. These values represent approximately 10% of the concentration contained in the lowest Youden pair.

Detectable background levels were reported for the different compounds in the various water types, but with more frequency in the wastewater samples. Except in a few isolated cases these spurious results were reported at concentrations that were insignificant when compared to the concentration level of the lowest Youden pair.

EFFECTS ACROSS WATER TYPE

The multiplicative model (Equation 10) was fitted separately to the data for each compound in order to test for the effects due to water type. These

analyses are summarized in Table 14. The detailed analyses of variance tables supporting these results are presented in Tables A-29 to 36.

TABLE 14. SUMMARY OF THE TEST FOR THE DIFFERENCES ACROSS WATER TYPES

Compound	Observed F-Value	P F > F OBS	Significant at the 5% Level	Significance Effect Established By 95% Confidence Intervals?
Hexachloroethane	2.05	0.0256	Yes	No
Hexachlorobutadiene	1.98	0.0330	Yes	No
2-Chloronaphthalene	3.12	0.0007	Yes	No
1,2-Dichlorobenzene	2.41	0.0084	Yes	No
1,3-Dichlorobenzene	2.37	0.0097	Yes	No
1,4-Dichlorobenzene	1.22	0.2776	No	-
1,2,4-Trichlorobenzene	0.88	0.5505	No	-
Hexachlorobenzene	1.65	0.0894	No	-

No practical significance established.

In all cases, there was no evidence of a statistically significant effect on accuracy or precision due to water type. In the cases of the first five compounds in Table 14 a statistically significant effect was established since $P(F>F\ OBS) < 0.05$; however, the simultaneous confidence intervals for $\ell n\ \beta j - \ell n\ \beta_1$ and $\gamma j - \gamma_1$ all included zero. The latter three compounds in Table 14 indicated no statistically significant effect since $P(F>F\ OBS) < 0.05$.

METHOD PROBLEMS AND RECOMMENDATIONS

Reviewing the reports, data sheets, and phone conversations showed that very few problems were encountered with the methods during the study. Three problems which occurred were:

1. One laboratory had a problem with the concentration of the extract using the Kuderna-Danish apparatus. The problem was an inability to concentrate the extract in the time frame specified by the method. The laboratory corrected the problem after being advised to (1) raise the temperature of the hot water bath; (2) lower the apparatus in the bath; and (3) check the column length of the Snyder column above the top ball and shorten it if necessary to reduce refluxing in the column.

2. One of the laboratories reported a problem in the quantitation of the chromatographic peaks with the use of a recording integrator. The

have had peaks near the peak of interest which changed the integration start or stop point from that of the standard. Many laboratories found satisfactory results using peak height measurements for quantitation. A warning or precaution about this problem should be placed in the EPA Method 612-Chlorinated Hydrocarbons.

In future interlaboratory studies, very detailed instruction should be given to the participating laboratories to ensure labeling of each chromatogram. In this study it was very difficult to interpret much of the raw chromatographic data because of inadequate labeling. Other points to be emphasized in future studies are that (a) blanks and spiked samples must be analyzed at the same sensitivity and (b) calculations and record keeping should be uniform or consistent to aid in data interpretation.

CONCLUSIONS

The statistical analyses performed by the IMVS computer programs indicate that EPA Method 612-Chlorinated Hydrocarbons is satisfactory for the analysis of the compounds studied over the concentration ranges and water types used in this method study. The IMVS computer program test for effect of water type also indicated that during EPA Method Study 22 there were no statistical significant differences between distilled water and the corresponding wastewater for any of the associated parameters. However, when applying the method, the analyst should first develop recovery and precision data on the wastewater type of concern at the concentrations determined or expected.

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APPENDIX A

TABLE A-1. CHLORINATED HYDROCARBONS IN MEK - RESULTS OF VERIFICATION AND STABILITY STUDY

	Ampul 1				Ampul 6			
	True Value	Day 0	Day 45	Day 90	True Value	Day 0	Day 45	Day 90
m-Dichlorobenzene	10.2	9.95	11.4	9.92	11.9	13.1	13.0	11.2
p-Dichlorobenzene	11.5	11.2	12.2	11.0	13.0	13.7	13.4	12.6
Hexachloroethane	0.512	0.501	0.524	0.544	0.592	0.614	0.591	0.640
o-Dichlorobenzene	14.9	14.3	17.4	14.5	17.8	18.9	21.4	17.5
Hexachlorobutadiene	1.56	1.52	1.71	1.52	1.84	1.89	1.98	1.83
1,2,4-Trichlorobenzene	7.54	7.39	8.78	8.12	8.64	8.85	10.2	9.77
2-Chloronaphthalene	10.7	10.6	12.6	9.60	9.55	9.76	11.8	9.30
Hexachlorobenzene	0.744	0.734	0.742	0.756	0.646	0.652	0.670	0.676

TABLE A-2. CHLORINATED HYDROCARBONS IN MEK - RESULTS OF VERIFICATION AND STABILITY STUDY

	Ampul 2				Ampul 5			
	True Value	Day 0	Day 45	Day 90	True Value	Day 0	Day 45	Day 90
m-Dichlorobenzene	25.5	25.2	26.0	26.5	29.7	30.1	28.9	32.7
p-Dichlorobenzene	86.2	84.3	90.9	83.1	97.2	96.5	100.	90.4
Hexachloroethane	1.28	1.25	1.46	1.48	1.48	1.47	1.60	1.67
o-Dichlorobenzene	74.5	73.7	84.0	72.3	88.8	88.4	96.5	82.3
Hexachlorobutadiene	11.7	11.5	12.0	11.3	13.8	13.7	13.4	12.8
1,2,4-Trichlorobenzene	18.9	18.7	21.1	20.5	21.6	21.7	22.6	23.2
2-Chloronaphthalene	80.4	78.9	96.7	74.9	71.6	72.3	89.3	62.9
Hexachlorobenzene	3.72	3.65	3.68	3.87	3.23	3.23	3.34	3.47

TABLE A-3. CHLORINATED HYDROCARBONS IN MEK - RESULTS OF VERIFICATION AND STABILITY STUDY

	Ampul 3				Ampul 4			
	True Value	Day 0	Day 45	Day 90	True Value	Day 0	Day 45	Day 90
m-Dichlorobenzene	102	100	110	97.9	119	118	121	118
p-Dichlorobenzene	144	143	187	135	162	159	159	153
Hexachloroethane	6.40	6.39	6.28	6.63	7.4	7.2	6.9	7.8
o-Dichlorobenzene	149	148	179	145	178	175	201	179
Hexachlorobutadiene	15.6	15.6	17.2	15.0	18.4	18.2	19.2	17.8
1,2,4-Trichlorobenzene	94.0	93.8	92.1	94.0	108	106	87	108
2-Chloronaphthalene	134	131	172	123	119	114	155	122
Hexachlorobenzene	7.44	7.26	7.17	7.64	6.46	6.19	6.62	6.80

TABLE A-4. PRECONFERENCE STUDY DATA SUMMARY - CHLORINATED HYDROCARBONS

	Ampul A				Ampul B			
	True Value	Mean Recovery	Std. Dev.	% Rel. Dev.	True Value	Mean Recovery	Std. Dev.	% Ref. Dev.
Hexachloroethane	2.0	2.3	0.5	21.7	2.4	2.1	0.1	4.8
Hexachlorobutadiene	6.2	3.4	1.6	47.1	7.4	4.1	1.9	46.3
2-Chloronapthalene	42.8	38.3	12.9	33.7	38.2	34.3	11.5	33.5
1,2-Dichlorobenzene	59.6	44.7	20.3	45.4	71.0	49.2	23.0	46.7
1,3-Dichlorobenzene	40.8	33.0	9.5	28.8	47.4	32.5	8.3	25.5
1,4-Dichlorobenzene	46.0	46.7	19.7	42.2	51.8	75.2	59.5	79.1
1,2,4-Trichlorobenzene	30.2	19.6	7.6	38.8	34.6	22.1	8.9	40.3
Hexachlorobenzene	3.0	2.5	0.7	28.0	2.6	2.2	0.7	31.8

Std. Dev. = Overall standard deviation

% Rel. Dev. = % Relative deviation

Concentrations in µg/L

TABLE A-5

ENVIRONMENTAL MONITORING AND SUPPORT LABORATORY
OFFICE OF RESEARCH AND DEVELOPMENT
ENVIRONMENTAL PROTECTION AGENCY

EPA METHOD VALIDATION STUDY-11 ENVIROSCI CHTDRCARS

RAW DATA FOR HEXACHLOROETHANE ANALYSIS BY WATER TYPE
LOW YOUDEN PAIR, UNITS - UG/L

	DISTILLED WATER		TAP WATER		SURFACE WATER		WASTE WATER 1		WASTE WATER 2		WASTE WATER 3	
AMPUL NO:	1	6	1	6	1	6	1	6	1	6	1	6
TRUE CONC:	1.02	1.18	1.02	1.18	1.02	1.18	1.02	1.18	1.02	1.18	1.02	1.18
LAB NUMBER												
1	0.56	0.70	0.71	0.97	0.75	0.78	0.64	0.80	0.50	0.70	0.74	0.60
2	0.24*	0.48*	0.33*	0.42*	0.49*	0.38*	0.40*	0.41*	0.46	0.66	0.44*	0.45*
3	0.45*	0.33*	0.32*	0.31*	0.52	0.53	0.65*	0.69*	0.09*	0.60*	0.47*	0.50*
4	1.10*	1.65*	3.37*	4.41*	1.28	1.50	1.51	2.32*	4.06*	6.86*	2.91*	4.10*
6	0.68	0.77	0.71	0.68	0.85	0.86	0.72	0.65	0.87	0.91	0.77	0.85
7	0.29*	0.40*	0.71	0.62	0.51	0.60	1.26	0.51	0.76	0.53	0.39	0.60
8	0.80	0.59	0.65	1.91*	0.47	3.46	0.44	0.52	0.66	0.55	0.51	0.72
9	0.65	0.91	0.53	0.60	0.80	0.67	0.83	1.18	0.68	1.06	2.88*	1.36*
10	0.18	0.64	0.05*	0.77	1.05	0.39	0.80	0.81	*	0.92	1.01	0.86
11	0.57	0.82	0.77	0.43	0.20	0.54	0.84	0.80	0.65	0.77	0.80	0.80
12	0.96	0.91	0.98	0.93	0.72	0.94	1.01	1.10	0.75	1.01	0.74	0.95
13	0.81	0.79	0.88	0.78	0.13*	0.23*	0.49	0.44	0.36	2.04*	0.60	0.79
14	0.59	0.72	0.72	0.78	0.60	0.73	1.02	0.96	0.43	0.50	.37	0.58
15	0.29	1.41	0.48	19.10*	0.91	3.32	1.73	1.40	0.88	0.82	2.83*	4.00*
17	0.81	0.96	0.74	0.90	0.85	0.95	0.69	0.69	0.92	1.27	0.85	0.79
18	7.78*	10.40*	7.79*	12.20*	8.55*	10.70*	8.74*	11.10*	8.74*	11.10*	8.29*	10.00*
19	0.88	0.95	0.69	0.93	0.84	1.50	1.15	1.13	0.29	1.21	0.87	0.87
20	1.25	1.35	0.83	1.17	1.23	1.31	1.16	1.20	0.93	1.00	0.80	0.90
21	2.40*	1.40	1.70*	1.50	2.60*	1.40	1.60*	2.50*	2.70*	3.60*	2.30*	1.90*
22	0.54	0.68	0.48	0.60	0.62	0.58	0.64	0.72	0.57	0.84	0.72	0.76

TABLE A-6

ENVIRONMENTAL MONITORING AND SUPPORT LABORATORY
OFFICE OF RESEARCH AND DEVELOPMENT
ENVIRONMENTAL PROTECTION AGENCY

EPA METHOD VALIDATION STUDY-IT ENVIROSCI CHTDRCARS

RAW DATA FOR HEXACHLOROETHANE ANALYSIS BY WATER TYPE
MEDIUM YOUDEN PAIR, UNITS - UG/L

	DISTILLED WATER		TAP WATER		SURFACE WATER		WASTE WATER 1		WASTE WATER 2		WASTE WATER 3	
AMPUL NO:	2	5	2	5	2	5	2	5	2	5	2	5
TRUE CONC:	2.56	2.96	2.56	2.96	2.56	2.96	2.56	2.96	2.56	2.96	2.56	2.96
LAB NUMBER												
1	1.97	1.72	1.27	2.29	1.70	2.04	1.34	2.10	1.36	4.54	1.77	1.45
2	0.89+	0.90+	0.81+	0.88+	1.04+	1.20+	1.03+	1.23+	0.91	1.62	1.15+	1.08+
3	1.00+	1.05+	0.85+	0.85+	1.30	1.25	1.00+	1.20+	1.00+	1.25+	0.40+	0.90+
4	4.32+	4.77+	11.70+	14.30+	4.56	7.00	6.71+	4.03	6.50+	7.30	6.96+	9.70+
6	1.99	2.46	1.81	1.93	2.03	2.60	1.82	2.25	2.42	2.53	2.08	2.57
7	0.78+	0.63+	2.73	0.87	1.57	2.40	2.34	2.51	0.31	1.49	1.75	2.46
8	1.17	1.02	0.51	2.35	0.59	2.52	1.55	2.46	0.95	2.25	1.12	1.81
9	1.32	3.75	1.41	6.65+	4.65	11.29+	2.44	13.91+	2.73	10.53+	3.71	10.46+
10	0.31	2.48	0.94	1.50	1.60	1.76	1.66	2.15	2.08	1.26	2.06	2.40
11	1.57	2.07	1.85	2.12	1.68	1.58	2.52	2.52	1.52	4.35	2.40	2.80
12	1.89	2.62	2.07	2.62	2.50	2.78	2.16	2.73	1.89	2.51	2.07	2.62
13	1.75	2.31	2.32	1.47	0.40+	0.08+	2.19	1.65	0.29	0.24	3.11	2.30
14	2.17	2.04	2.70	2.87	2.66	2.29	2.79	2.46	1.48	2.53	2.09	1.97
15	1.12	3.14	2.06	19.50+	1.51	3.45	2.01	3.12	2.08	2.00	7.92+	4.79+
17	2.00	2.20	1.90	2.30	0.95	2.25	1.99	2.19	2.17	2.67	2.45	2.15
18	29.20+	29.10+	13.30+	29.60+	28.10+	31.00+	31.00+	31.70+	31.00+	30.90+	28.90+	32.10+
19	2.14	2.41	1.71	2.19	2.87	3.20	2.71	4.43	1.31	4.10	1.61	3.49
20	3.25	3.35	2.63	3.85	3.20	3.80	2.60	3.00	3.00	3.20	2.50	3.20
21	3.30	1.80	5.20+	4.60	0.90	6.20	7.50+	4.30+	6.70+	7.40+	4.70+	6.90+
22	1.69	1.09	1.97	0.87	1.85	1.75	1.72	1.73	1.36	3.27	1.35	1.44

TABLE A-7

ENVIRONMENTAL MONITORING AND SUPPORT LABORATORY
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ENVIRONMENTAL PROTECTION AGENCY

EPA METHOD VALIDATION STUDY-IT ENVIROSCI CHTDRCARS

RAW DATA FOR HEXACHLOROETHANE ANALYSIS BY WATER TYPE
HIGH YOUDEN PAIR, UNITS - UG/L

	DISTILLED WATER		TAP WATER		SURFACE WATER		WASTE WATER 1		WASTE WATER 2		WASTE WATER 3	
AMPUL NO:	3	4	3	4	3	4	3	4	3	4	3	4
TRUE CONC:	12.80	14.80	12.80	14.80	12.80	14.80	12.80	14.80	12.80	14.80	12.80	14.80
LAB NUMBER												
1	6.50	9.31	7.92	10.10	8.10	8.38	7.60	8.88	7.47	8.52	6.46	8.66
2	3.90+	5.70+	4.91+	4.92+	5.81+	7.85+	6.37+	4.71+	5.76	6.26	4.22+	5.37+
3	3.25+	6.10+	4.25+	3.50+	6.90	8.25	4.05+	5.55+	3.30+	5.10+	4.25+	4.75+
4	25.50+	25.10+	15.60+	23.60+	10.30	12.70	10.90	8.44	8.44	12.00	11.80+	21.00+
6	7.92	9.26	11.80	13.20	15.90	13.10	11.60	14.20	11.50	13.20	11.20	13.50
7	6.52+	2.64+	8.27	9.14	9.43	10.70	12.70	9.68	7.94	10.10	13.30	15.20
8	21.20+	18.90	16.50	4.09	6.70	4.79	5.95	4.90	5.16	5.61	11.40	5.20
9	11.77	14.11	9.45	11.09	15.23	17.34	12.31	15.09	6.91	9.74	7.89	6.50
10	2.86	0.45	8.48	6.91	1.17	7.72	9.30	10.90	13.00	7.08	10.10	10.70
11	10.40	11.10	*	8.34	9.87	7.25	11.50	12.20	12.80	14.40	11.70	14.80
12	7.91	8.41	9.17	8.95	7.60	8.77	7.61	8.47	7.44	8.20	6.91	8.85
13	11.10	11.90	11.20	11.40	2.74+	3.04+	12.20	13.10	1.72	1.60	12.30	13.80
14	9.04	7.92	11.60	13.30	10.60	11.30	10.60	11.20	7.48	11.40	9.25	9.06
15	9.12	11.60	9.12	15.40	8.54	15.50	25.10+	16.70	23.20+	12.70	45.80+	26.20+
17	8.80	10.10	9.00	9.90	8.95	10.50	9.29	13.70	10.40	11.30	9.95	10.20
18	128.00+	130.00+	133.00+	137.00+	125.00+	144.00+	122.00+	136.00+	122.00+	136.00+	135.00+	145.00+
19	10.30	10.70	7.74	10.10	*	14.90	13.40	1.04	6.41	7.48	25.40+	11.90
20	15.40	17.80	11.40	16.40	15.50	21.20	13.50	15.80	12.00	15.10	11.10	15.20
21	4.50	12.30	14.40	14.50	30.70+	17.90	23.50+	26.30+	31.70+	25.90+	29.70+	29.80+
22	9.99	10.50	9.16	11.20	9.63	11.50	9.73	12.20	10.70	11.90	9.94	13.40

TABLE A-8.

ENVIRONMENTAL MONITORING AND SUPPORT LABORATORY
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ENVIRONMENTAL PROTECTION AGENCY

EPA METHOD VALIDATION STUDY-IT ENVIROSCI CHTDRCARS

RAW DATA FOR HEXACHLOROBUTADIENE ANALYSIS BY WATER TYPE
LOW YOUDEN PAIR, UNITS - UG/L

	DISTILLED WATER		TAP WATER		SURFACE WATER		WASTE WATER 1		WASTE WATER 2		WASTE WATER 3	
AMPUL NO:	1	6	1	6	1	6	1	6	1	6	1	6
TRUE CONC:	3.12	3.68	3.12	3.68	3.12	3.68	3.12	3.68	3.12	3.68	3.12	3.68
LAB NUMBER												
1	1.43	1.93	2.21	2.66	2.14	2.18	1.63	2.33	1.29	2.08	2.08	1.39
2	0.62	1.43	1.02	1.29	1.29	1.13	1.31	1.48	0.79	1.60	1.33	1.53
3	1.17	0.67	0.61*	0.64*	1.16	1.21	1.24*	1.28*	0.66*	1.27*	0.86*	1.12*
4	1.92	2.62	6.24*	6.00	2.34	2.47	2.14	5.26	6.86	11.80*	4.50	6.72*
6	1.76	2.13	2.07	1.88	2.30	2.48	1.80	1.90	2.53	3.15	2.35	2.67
7	0.64*	0.78*	1.99	1.92	1.63	1.65	2.53	1.35	1.29	1.57	0.97	1.39
8	0.00*	3.98	3.62	4.28	2.40	3.51	1.77	0.80	4.96	1.45	4.52	3.46
9	1.07	3.26	1.43	2.86	1.63	4.36	2.11	3.30	0.96	3.11	3.88	2.11
10	0.78	1.56	0.40	1.67	2.29	0.67	1.95	2.60	*	2.26	3.54	2.14
11	0.80	1.50	0.89*	0.70*	0.36*	0.91*	1.50	1.40	1.36	1.70	1.60	2.00
12	2.06	2.91	3.34	2.72	2.12	2.64	2.77	3.57	2.39	3.03	2.73	3.73
13	3.22	2.57	1.68	1.95	0.51*	0.93*	1.79	2.42	0.67*	0.03*	2.04	2.75
14	22.30*	23.00*	29.50*	33.30*	22.90*	27.00*	19.40*	24.20*	7.30*	17.70*	17.40*	21.20*
15	0.12*	0.53*	0.16*	0.94*	0.29*	1.45*	0.70*	0.52*	0.08*	0.06*	0.62*	0.80*
17	3.32	4.16	3.50	4.65	3.36	4.66	4.00*	4.50*	4.40*	4.88*	4.24	3.70
18	28.20*	361.00*	28.10*	383.00*	31.10*	377.00*	31.20*	377.00*	31.20*	377.00*	31.50*	357.00*
19	1.96	2.10	1.66	2.21	2.08	3.39	2.09	1.28	0.75	3.52	2.71	2.10
20	3.45	4.35	2.52	3.80	3.50*	4.14*	3.30	3.90	3.20	3.30	2.50	3.60
21	1.70	2.70	1.50	1.30	11.30*	2.30	2.90	4.00	3.30	4.00	3.40	3.20
22	1.65	2.05	1.48	1.92	1.83	1.63	2.77	1.60	1.92	2.42	2.59	2.64

TABLE A-9.

ENVIRONMENTAL MONITORING AND SUPPORT LABORATORY
OFFICE OF RESEARCH AND DEVELOPMENT
ENVIRONMENTAL PROTECTION AGENCY

EPA METHOD VALIDATION STUDY-IT ENVIROSCI CHTDRCARS

RAW DATA FOR HEXACHLOROBUTADIENE ANALYSIS BY WATER TYPE
MEDIUM YOUDEN PAIR, UNITS - UG/L

	DISTILLED WATER		TAP WATER		SURFACE WATER		WASTE WATER 1		WASTE WATER 2		WASTE WATER 3	
AMPUL NO:	2	5	2	5	2	5	2	5	2	5	2	5
TRUE CONC:	23.40	27.60	23.40	27.60	23.40	27.60	23.40	27.60	23.40	27.60	23.40	27.60
LAB NUMBER												
1	15.20	13.50	11.30	18.70	13.90	16.50	10.80	16.40	11.50	15.60	14.20	11.00
2	8.33	7.25	7.86	7.19	9.26	10.30	10.60	12.80	5.99	13.50	11.70	11.30
3	8.05	9.35	4.20+	7.05+	11.50	8.20	4.50+	8.25+	7.32+	8.82+	2.20+	5.80+
4	11.90	16.80	49.20+	20.30	12.60	22.00	14.20	8.83	14.70	20.60	10.40	22.30
6	16.60	23.20	14.70	15.40	17.40	22.40	15.70	20.70	22.40	24.60	20.00	27.10
7	5.48+	2.81+	19.70	5.78	12.90	18.00	17.80	15.10	2.21	12.70	12.80	19.70
8	10.10	8.99	4.78	25.20	6.27	22.80	7.21	1.57	7.90	12.50	8.05	27.40
9	19.46	34.85	14.86	30.10	16.82	28.60	17.30	32.72	8.40	23.72	6.59	17.81
10	1.70	15.60	5.40	10.00	13.60	9.62	17.70	25.20	27.60	9.58	23.40	28.20
11	8.66	12.50	4.69+	12.30+	10.90+	8.64+	15.60	16.20	10.80	24.70	15.60	19.20
12	11.40	14.10	14.20	16.80	15.90	17.00	14.60	16.40	13.90	15.60	14.30	15.70
13	19.70	24.20	25.50	34.60	7.53+	0.99+	21.80	18.40	3.01+	3.26+	21.70	31.10
14	170.00+	165.00+	256.00+	258.00+	189.00+	177.00+	204.00+	233.00+	107.00+	188.00+	167.00+	152.00+
15	0.76+	3.39+	2.26+	1.33+	1.58+	5.95+	1.58+	3.45+	0.37+	0.59+	5.80+	2.57+
17	26.40	29.30	24.20	31.80	12.20	32.30	28.60+	33.60+	31.50+	35.70+	27.50	29.70
18	212.00+	245.00+	227.00+	251.00+	226.00+	258.00+	236.00+	258.00+	236.00+	257.00+	232.00+	266.00+
19	14.70	24.00	11.00	16.20	21.90	21.90	16.70	25.90	7.44	26.50	8.16	22.30
20	25.30	34.70	20.70	31.60	28.20+	35.00+	21.20	26.70	24.10	28.30	23.30	29.40
21	10.50	8.40	17.50	15.80	39.00+	22.00	33.30+	18.50	27.00	33.50	21.20	29.10
22	14.30	9.35	16.70	5.03	15.40	18.30	14.30	20.40	12.00	24.60	12.60	13.50

TABLE A-10.

ENVIRONMENTAL MONITORING AND SUPPORT LABORATORY
OFFICE OF RESEARCH AND DEVELOPMENT
ENVIRONMENTAL PROTECTION AGENCY

EPA METHOD VALIDATION STUDY-II ENVIROSCI CHTDRCARS

RAW DATA FOR HEXACHLOROBUTADIENE ANALYSIS BY WATER TYPE
HIGH YOUDEN PAIR, UNITS - UG/L

	DISTILLED WATER		TAP WATER		SURFACE WATER		WASTE WATER 1		WASTE WATER 2		WASTE WATER 3	
AMPUL NO:	3	4	3	4	3	4	3	4	3	4	3	4
TRUE CONC:	32.20	36.80	32.20	36.80	32.20	36.80	32.20	36.80	32.20	36.80	32.20	36.80
LAB NUMBER												
1	12.70	20.20	14.70	22.90	17.10	17.70	15.80	21.10	16.70	18.80	12.50	18.60
2	9.28	12.90	11.20	11.40	12.30	16.70	15.40	13.10	12.10	14.30	10.30	15.30
3	7.80	13.00	6.65+	4.90+	13.40	23.40	7.95+	16.10+	5.02+	8.37+	8.20+	8.50+
4	36.20	41.20	21.50	32.60	16.30	18.30	13.50	15.70	12.00	19.60	16.60	40.00
6	19.40	20.80	22.00	24.00	26.70	41.00	22.80	28.70	30.30	30.00	24.20	27.90
7	13.00+	3.18+	17.00	18.50	19.00	21.30	27.60	22.90	17.10	27.80	26.80	31.60
8	13.30	11.10	10.40	23.40	6.79	28.40	16.60	10.30	8.10	20.70	7.67	15.80
9	29.53	30.15	23.36	25.98	16.44	21.43	15.74	24.62	18.42	19.24	12.51	18.73
10	4.26	0.62	14.90	12.60	2.56	12.50	20.80	25.20	20.60	16.50	22.90	23.70
11	12.70	16.90	*	7.86+	11.90+	9.17+	19.90	22.40	24.20	21.90	19.70	24.80
12	16.50	18.20	17.20	19.10	16.20	19.00	16.60	18.00	15.40	18.40	14.90	18.90
13	30.70	34.50	31.80	33.80	8.64+	9.62+	34.00	39.90	3.25+	2.77+	35.80	43.40
14	220.00+	177.00+	310.00+	370.00+	242.00+	296.00+	240.00+	259.00+	176.00+	289.00+	218.00+	220.00+
15	1.71+	3.13+	2.58+	4.86+	2.43+	5.01+	6.72+	1.37+	1.54+	0.39+	9.45+	4.93+
17	36.00	37.30	34.00	40.60	37.00	42.40	37.40+	53.40+	42.00+	48.40+	37.00	41.60
18	290.00+	302.00+	302.00+	315.00+	287.00+	336.00+	280.00+	320.00+	280.00+	320.00+	310.00+	340.00+
19	21.60	18.50	14.30	19.40	*	26.60	27.30	1.05	12.50	12.10	15.70	21.30
20	34.30	40.80	24.50	37.20	37.50+	48.20+	31.60	37.30	22.40	33.10	25.00	38.10
21	4.50	10.50	13.70	11.10	35.30	17.60	35.00	39.60	39.60	35.70	38.30	42.70
22	22.20	24.60	20.20	25.30	20.90	27.20	23.60	30.00	26.40	26.80	26.90	30.90

TABLE A-11.

ENVIRONMENTAL MONITORING AND SUPPORT LABORATORY
OFFICE OF RESEARCH AND DEVELOPMENT
ENVIRONMENTAL PROTECTION AGENCY

EPA METHOD VALIDATION STUDY-IT ENVIROSCI CHTDRCARS

RAW DATA FOR 2-CHLORONAPHTHALENE ANALYSIS BY WATER TYPE
LOW YOUDEN PAIR, UNITS - UG/L

	DISTILLED WATER		TAP WATER		SURFACE WATER		WASTE WATER 1		WASTE WATER 2		WASTE WATER 3	
AMPUL NO:	1	6	1	6	1	6	1	6	1	6	1	6
TRUE CONC:	21.40	19.10	21.40	19.10	21.40	19.10	21.40	19.10	21.40	19.10	21.40	19.10
LAB NUMBER												
1	16.50	17.30	16.90	16.70	18.30	16.20	15.90	21.20	24.60	31.50	17.60	15.50
2	10.70	16.80	11.00+	7.89+	20.40	18.20	9.53+	7.85+	18.90	17.80	16.50	14.80
3	15.10	12.40	13.80	12.40	14.80	14.00	28.50	89.30	15.10	15.20	10.90	13.30
4	21.00	21.20	52.80+	24.10	20.90	18.20	45.10	37.90	22.70	0.00+	26.60	24.70
6	20.10	17.20	21.10	17.60	26.90	14.80	16.40	20.60	49.90+	41.00	23.50	24.90
7	17.20	22.30	21.00	16.90	17.90	13.10	20.00	15.10	15.40	15.80	16.80	16.30
8	23.90	17.20	23.70	18.80	28.50	28.20	28.40	31.90	20.40	45.70	30.00+	340.00+
9	14.86	22.43	15.01	15.63	18.94	25.18	21.88	16.12	12.52	32.69	24.33	32.84
10	11.90	18.10	11.00	18.40	21.10	15.80	23.10	20.80	*	18.30	32.10	6.20
11	19.50	15.20	18.50	15.90	36.90+	17.60+	13.20	10.80	22.50	16.30	21.20	18.00
12	20.90	17.30	24.40	18.40	26.20	18.40	26.40	20.60	15.40	11.90	18.70	*
13	0.69+	2.33+	30.10	17.60	*	*	7.37	*	24.20	10.70	11.30	15.60
14	19.20	21.50	22.00+	20.70+	22.70	21.20	24.60	28.80	21.60	20.30	22.20	14.50
15	9.00	140.00+	15.00	160.00+	15.00	184.00+	9.00	90.00	6.00	41.00	3.00	147.00+
17	14.70	2.20	19.20	16.00	8.50	15.00	17.50	6.00	19.00	15.00	5.00	4.40
18	0.00+	0.00+	0.00+	0.00+	0.00+	0.00+	11.80	0.00+	187.00+	159.00+	0.00+	0.00+
19	39.30+	36.10	14.10	11.80	16.90	17.00	30.60	31.30	8.12	17.80	9.97	13.40
20	21.80	22.10	22.50+	21.00+	24.40	22.00	22.70	23.30	4.60+	10.60+	13.40	17.10
21	99.60+	28.00	27.70	20.40	30.80+	26.50+	17.60	34.70	103.30+	108.00+	19.30	21.00
22	20.00	16.60	21.90	19.80	21.00	17.70	33.60	19.00	22.10	57.30	21.80	25.50

TABLE A-12.

ENVIRONMENTAL MONITORING AND SUPPORT LABORATORY
OFFICE OF RESEARCH AND DEVELOPMENT
ENVIRONMENTAL PROTECTION AGENCY

EPA METHOD VALIDATION STUDY-11 ENVIROSCI CHTDRCARS

RAW DATA FOR 2-CHLORONAPHTHALENE ANALYSIS BY WATER TYPE
MEDIUM YOUDEN PAIR, UNITS - UG/L

	DISTILLED WATER		TAP WATER		SURFACE WATER		WASTE WATER 1		WASTE WATER 2		WASTE WATER 3	
AMPUL NO:	2	5	2	5	2	5	2	5	2	5	2	5
TRUE CONC:	161.00	143.00	161.00	143.00	161.00	143.00	161.00	143.00	161.00	143.00	161.00	143.00
LAB NUMBER												
1	132.00	125.00	134.00	131.00	129.00	128.00	101.00	117.00	111.00	113.00	134.00	107.00
2	88.20	104.00	63.70*	50.30*	128.00	117.00	97.10*	88.20*	101.00	113.00	134.00	98.30
3	107.00	90.60	100.00	110.00	100.00	105.00	116.00	108.00	129.00	101.00	53.00	47.50
4	129.00	158.00	149.00	141.00	150.00	226.00*	177.00	92.10	104.00	147.00	120.00	101.00
6	137.00	124.00	146.00	118.00	140.00	115.00	136.00	126.00	152.00	137.00	154.00	134.00
7	141.00	147.00	194.00	92.00	98.40	110.00	140.00	133.00	139.00	110.00	116.00	104.00
8	134.00	119.00	123.00	94.00	128.00	115.00	135.00	202.00	99.40	185.00	593.00*	530.00*
9	119.59	189.62	89.64	168.41	99.41	171.64	136.92	151.84	69.71	148.89	115.81	172.62
10	41.40	105.00	120.00	116.00	126.00	117.00	154.00	158.00	132.00	91.00	86.40	122.00
11	199.00	160.00	137.00	145.00	165.00*	151.00*	105.00	92.80	134.00	197.00	190.00	140.00
12	104.00	93.70	91.50	91.10	107.00	91.10	101.00	107.00	80.50	82.20	96.30	88.20
13	48.10*	38.10*	162.00	160.00	3.07*	3.60*	144.00	*	62.40	59.30	137.00	119.00
14	169.00	132.00	174.00*	141.00*	163.00	98.40	160.00	166.00	156.00	153.00	165.00	132.00
15	74.00	71.00	85.00	59.00	89.00	80.00	23.00*	26.00	90.00	122.00	60.00	51.00
17	97.00	23.30	127.00	120.00	145.00	120.00	145.00	20.00	140.00	120.00	108.00	112.00
18	1200.00*	0.00*	0.00*	0.00*	2.33*	57.80*	157.00	0.00*	1190.00*	982.00*	0.00*	0.00*
19	221.00	86.70	57.40	52.30	91.30	104.00	134.00	134.00	111.00	78.30	110.00	96.60
20	146.10	138.90	160.60*	145.10*	148.30	152.30	163.10	142.10	95.10*	103.60*	125.00	107.50
21	125.40	91.00	131.00	114.10	180.00*	159.00*	48.60*	103.60	188.40*	263.60*	111.40	128.80
22	140.00	98.90	140.00	55.00	134.40	140.00	154.60	95.60	153.70	174.10	142.40	115.40

TABLE A-13.

ENVIRONMENTAL MONITORING AND SUPPORT LABORATORY
OFFICE OF RESEARCH AND DEVELOPMENT
ENVIRONMENTAL PROTECTION AGENCY

EPA METHOD VALIDATION STUDY-IT ENVIROSCI CHTDRCARS

RAW DATA FOR 2-CHLORONAPHTHALENE ANALYSIS BY WATER TYPE
HIGH YOUDEN PAIR, UNITS - UG/L

	DISTILLED WATER		TAP WATER		SURFACE WATER		WASTE WATER 1		WASTE WATER 2		WASTE WATER 3	
AMPUL NO:	3	4	3	4	3	4	3	4	3	4	3	4
TRUE CONC:	268.00	238.00	268.00	238.00	263.00	238.00	268.00	238.00	268.00	238.00	268.00	238.00
LAB NUMBER												
1	231.00	218.00	228.00	229.00	214.00	222.00	229.00	233.00	224.00	216.00	183.00	187.00
2	134.00	168.00	118.00*	101.00*	219.00	195.00	162.00*	139.00*	191.00	173.00	187.00	171.00
3	144.00	132.00	163.00	142.00	213.00	181.00	190.00	152.00	138.00	193.00	155.00	124.00
4	248.00	182.00	242.00	204.00	228.00	206.00	207.00	175.00	179.00	160.00	120.00	182.00
6	222.00	206.00	217.00	200.00	228.00	199.00	228.00	207.00	241.00	240.00	258.00	245.00
7	233.00	183.00	253.00	260.00	169.00	181.00	225.00	138.00	211.00	214.00	229.00	181.00
8	201.00	225.00	173.00	127.00	178.00	160.00	258.00	297.00	199.00	415.00*	390.00*	206.00*
9	255.82	222.95	156.10	187.26	187.23	243.42	201.20	143.31	125.67	142.42	132.34	168.57
10	128.00	24.70	210.00	189.00	218.00	195.00	229.00	246.00	218.00	182.00	235.00	207.00
11	341.00	284.00	*	167.00	424.00*	280.00*	313.00	161.00	314.00	234.00	310.00	269.00
12	151.00	135.00	159.00	138.00	148.00	141.00	146.00	139.00	145.00	145.00	113.00	173.00
13	100.00*	92.00*	227.00	228.00	21.70*	6.20*	266.00	247.00	130.00	105.00	282.00	240.00
14	239.00	176.00	268.00*	238.00*	269.00	209.00	266.00	206.00	251.00	208.00	243.00	217.00
15	142.00	102.00	123.00	103.00	132.00	124.00	216.00	146.00	54.00	33.00*	129.00	81.00
17	188.00	62.00	217.00	186.00	172.00	194.00	213.00	171.00	235.00	177.00	182.00	172.00
18	0.00*	3.44	0.00*	0.00*	0.00*	0.00*	16.80*	15.10	1730.00*	1500.00*	0.00*	0.00*
19	193.00	410.00	178.00	102.00	*	162.00	188.00	152.00	166.00	157.00	124.00	126.00
20	247.90	209.90	242.40*	236.20*	261.70	226.80	270.20	155.40	116.80*	125.00*	176.80	210.90
21	138.60	134.70	209.20	190.00	263.00*	217.50*	215.50	111.70	350.00*	280.50*	251.10	122.90
22	215.20	225.40	234.20	216.70	229.80	217.40	215.40	244.40	268.00	213.80	233.80	215.50

TABLE A-14.

ENVIRONMENTAL MONITORING AND SUPPORT LABORATORY
OFFICE OF RESEARCH AND DEVELOPMENT
ENVIRONMENTAL PROTECTION AGENCY

EPA METHOD VALIDATION STUDY-11 ENVIROSCI CHLORCARS

RAW DATA FOR 1,2-DICHLOROBENZENE ANALYSIS BY WATER TYPE
LOW YOUDEN PAIR, UNITS - UG/L

	DISTILLED WATER		TAP WATER		SURFACE WATER		WASTE WATER 1		WASTE WATER 2		WASTE WATER 3	
AMPUL NO:	1	6	1	6	1	6	1	6	1	6	1	6
TRUE CONC:	29.80	35.60	29.80	35.60	29.80	35.60	29.80	35.60	29.80	35.60	29.80	35.60
LAB NUMBER												
1	20.20	28.70	24.30	34.90	23.50	28.90	19.70	41.50	22.70	30.30	29.60	31.60
2	21.20	40.60	28.50	32.90	50.50*	46.40*	28.40	31.50	31.70	45.30	36.40	35.20
3	17.65	19.00	16.30	18.90	18.20	23.00	15.70	17.90	6.88	21.20	17.50*	18.20*
4	13.00	26.20	43.10	72.00	25.70	24.30	20.40	41.40	26.00	0.00*	44.00	86.90
6	20.70	25.80	23.40	28.20	26.10	33.60	17.80	13.00	121.00*	53.80	127.00*	53.90
7	15.00	23.10	23.10	22.90	20.30	25.90	25.90	20.30	23.90	28.20	19.70	26.90
8	83.10*	43.30	25.30	66.00	30.50	503.00*	2.73	19.40	44.80	36.40	37.00	58.30
9	24.15	102.27*	28.21	88.04	31.42	73.09*	32.35	59.81	24.53	64.39	33.63	51.64
10	12.60	27.30	9.39	26.50	26.40	19.10	22.30	24.70	*	26.10	26.00	22.80
11	25.30	31.60	47.00	20.20	12.70	20.30	26.00	22.00	24.70	32.90	28.80	38.80
12	23.00	34.20	60.80	43.30	26.70	41.40	47.40	36.10	32.80	40.00	*	13.20
13	23.80	32.50	24.30	26.40	4.54*	7.92*	14.50	22.00	19.50*	10.40*	20.70	29.60
14	34.80	37.70	32.50	89.90	31.50	31.30	35.30	51.10	26.90	29.80	19.90	61.70
15	4.00*	8.00*	5.00*	11.00*	8.90*	15.00*	3.00*	8.00*	0.00*	0.00*	20.00	32.00
17	22.20	27.70	23.70	30.50	24.70	29.40	23.40	27.00	23.30	31.20	23.00	26.00
18	183.00*	202.00*	172.00*	244.00*	196.00*	232.00*	196.00*	215.00*	196.00*	215.00*	191.00*	203.00*
19	3.41*	3.99*	2.86*	3.07*	3.56*	5.28*	1.32*	3.67*	1.52*	7.69*	3.51*	4.05*
20	32.90	38.50	25.00	45.60	24.50	25.00	23.10	31.00	21.30	29.80	27.70	31.10
21	103.70*	86.40*	57.90*	171.90*	103.50*	77.80*	51.80*	68.40*	*	*	102.80*	67.90*
22	34.30	40.40	32.00	35.80	35.00	37.50	34.70	26.50	31.30	311.00*	35.30	44.30

TABLE A-15.

ENVIRONMENTAL MONITORING AND SUPPORT LABORATORY
OFFICE OF RESEARCH AND DEVELOPMENT
ENVIRONMENTAL PROTECTION AGENCY

EPA METHOD VALIDATION STUDY-IT ENVIROSCI CHLORCARS

RAW DATA FOR 1,2-DICHLOROBENZENE ANALYSIS BY WATER TYPE
MEDIUM YOUDEN PAIR, UNITS - UG/L

	DISTILLED WATER		TAP WATER		SURFACE WATER		WASTE WATER 1		WASTE WATER 2		WASTE WATER 3	
AMPUL NO:	2	5	2	5	2	5	2	5	2	5	2	5
TRUE CONC:	149.00	178.00	149.00	178.00	149.00	178.00	149.00	178.00	149.00	178.00	149.00	178.00
LAB NUMBER												
1	115.00	140.00	108.00	158.00	121.00	148.00	81.80	175.00	94.80	169.00	126.00	124.00
2	172.00	252.00	139.00	220.00	262.00+	299.00+	171.00	197.00	161.00	277.00	181.00	216.00
3	76.30	95.30	93.80	95.30	78.40	93.20	82.70	90.00	82.70	99.20	42.20+	73.90+
4	132.00	126.00	276.00	273.00	103.00	157.00	148.00	99.20	80.00	157.00	159.00	203.00
6	111.00	132.00	111.00	131.00	119.00	156.00	111.00	140.00	161.00	169.00	145.00	169.00
7	71.10	83.20	130.00	81.60	85.10	125.00	94.80	137.00	102.00	116.00	104.00	121.00
8	132.00	106.00	69.90	321.00	70.20	248.00	166.00	273.00	114.00	219.00	87.00	215.00
9	185.65	250.87	189.53	210.10	143.41	195.63	147.42	167.31	167.25	198.16	149.49	221.81
10	25.40	123.00	87.20	116.00	100.00	122.00	99.80	128.00	123.00	95.40	132.00	139.00
11	155.00	203.00	200.00	138.00	121.00	113.00	148.00	208.00	110.00	285.00	177.00	268.00
12	166.00	165.00	129.00	151.00	135.00	143.00	106.00	131.00	98.20	129.00	84.10	116.00
13	121.10	160.40	145.00	93.50	20.40+	10.34+	137.00	124.00	42.10+	48.70+	136.70	149.00
14	177.00	171.00	195.00	198.00	178.00	91.20	175.00	169.00	125.00	197.00	178.00	216.00
15	26.00+	54.00+	6.00+	5.00+	29.00+	38.00+	23.00+	66.00+	72.50+	0.00+	73.00	78.00
17	109.00	127.00	120.00	146.00	30.00	132.00	112.00	141.00	118.00	138.00	120.00	135.00
18	858.00+	905.00+	900.00+	912.00+	886.00+	934.00+	999.00+	936.00+	999.00+	936.00+	900.00+	974.00+
19	14.10+	28.20+	11.20+	17.10+	23.30+	24.70+	12.80+	24.00+	7.54+	35.90+	13.10+	17.10+
20	145.90	182.50	142.40	229.30	139.10	171.60	129.50	146.50	86.10	135.60	125.60	173.00
21	232.80	205.00	319.90+	353.60+	457.80+	381.90+	372.00+	207.60+	+	+	243.60+	354.90+
22	136.20	117.60	148.30	144.60	138.20	144.80	122.70	144.10	106.00	141.90	121.60	124.00

TABLE A-16.

ENVIRONMENTAL MONITORING AND SUPPORT LABORATORY
OFFICE OF RESEARCH AND DEVELOPMENT
ENVIRONMENTAL PROTECTION AGENCY

EPA METHOD VALIDATION STUDY-1T ENVIROSCI CHTDRCARS

RAW DATA FOR 1,2-DICHLOROBENZENE ANALYSIS BY WATER TYPE
HIGH YOUDEN PAIR. UNITS - UG/L

	DISTILLED WATER		TAP WATER		SURFACE WATER		WASTE WATER 1		WASTE WATER 2		WASTE WATER 3	
AMPUL NO:	3	4	3	4	3	4	3	4	3	4	3	4
TRUE CONC:	298.00	356.00	298.00	356.00	298.00	356.00	298.00	356.00	298.00	356.00	298.00	356.00
LAB NUMBER												
1	173.00	282.00	247.00	286.00	234.00	256.00	266.00	303.00	223.00	261.00	252.00	281.00
2	228.00	524.00	348.00	380.00	491.00*	636.00*	350.00	323.00	293.00	360.00	318.00	209.00
3	93.30	201.00	165.00	164.00	173.00	202.00	126.00	156.00	112.00	210.00	141.00*	148.00*
4	395.00	439.00	250.00	440.00	154.00	343.00	183.00	138.00	30.00	139.00	192.00	413.00
6	222.00	233.00	245.00	273.00	287.00	350.00	268.00	331.00	296.00	374.00	274.00	343.00
7	222.00	179.00	212.00	283.00	250.00	314.00	277.00	254.00	263.00	327.00	334.00	396.00
8	77.10	159.00	3.27*	268.00	80.00	322.00	399.00	365.00	158.00	414.00	93.40	402.00
9	353.41	452.55	294.11	308.98	268.30	291.49	225.24	282.03	205.58	225.81	261.54	290.19
10	105.00	12.70	200.00	183.00	126.00	229.00	203.00	248.00	244.00	184.00	217.00	253.00
11	405.00	463.00	*	285.00	419.00	264.00	323.00	418.00	486.00	443.00	383.00	519.00
12	219.00	266.00	234.00	298.00	181.00	285.00	205.00	298.00	222.00	243.00	120.00	281.00
13	158.50	189.60	131.90	147.10	63.10*	75.10*	135.20	151.70	90.90*	88.10*	153.90	162.10
14	327.00	281.00	372.00	443.00	384.00	382.00	320.00	376.00	291.00	451.00	435.00	365.00
15	79.00*	76.00*	40.00*	38.00*	42.00*	62.00*	86.00*	56.00*	73.50*	75.00*	214.00	161.00
17	207.00	257.00	233.00	255.00	228.00	257.00	230.00	296.00	231.00	270.00	220.00	270.00
18	1820.00*	1660.00*	2150.00*	1850.00*	1540.00*	1840.00*	1500.00*	1690.00*	1500.00*	1690.00*	1600.00*	1870.00*
19	99.80*	30.70*	27.00*	32.30*	*	47.60*	38.90*	1.28*	18.20*	21.50*	38.50*	41.90*
20	284.10	401.90	303.00	405.60	305.70	452.10	296.00	288.50	202.90	253.50	252.10	316.20
21	203.40	391.80	469.20*	518.80*	767.20*	647.90*	522.00*	591.80*	*	455.10*	669.80*	684.30*
22	320.40	376.20	307.70	284.50	313.50	390.00	305.00	387.00	338.20	399.40	325.90	395.90

TABLE A-17.

ENVIRONMENTAL MONITORING AND SUPPORT LABORATORY
OFFICE OF RESEARCH AND DEVELOPMENT
ENVIRONMENTAL PROTECTION AGENCY

EPA METHOD VALIDATION STUDY-IT ENVIROSCI CHLORCARS

RAW DATA FOR 1,3-DICHLOROBENZENE ANALYSIS BY WATER TYPE
LOW YOUDEN PAIR, UNITS - UG/L

	DISTILLED WATER		TAP WATER		SURFACE WATER		WASTE WATER 1		WASTE WATER 2		WASTE WATER 3	
AMPUL NO:	1	6	1	6	1	6	1	6	1	6	1	6
TRUE CONC:	20.40	23.80	20.40	23.80	20.40	23.80	20.40	23.80	20.40	23.80	20.40	23.80
LAB NUMBER												
1	16.40	22.30	22.40	21.60	19.80	19.70	21.20	24.00	14.40	18.10	18.30	16.30
2	8.85	15.40	12.90	17.40	15.90	13.40	3.46	*	14.30	20.00	15.60	12.50
3	17.00	15.10	13.70	14.70	15.20	20.90	20.70	21.20	4.00	22.50	28.90	32.40
4	15.60	18.90	40.60*	52.80*	18.60	23.10	30.70	24.30	61.20*	98.80*	27.60	54.60*
6	17.50	19.50	16.50	15.60	20.70	19.30	*	*	17.00	14.00	17.60	17.20
7	11.60	20.20	21.20	16.90	16.30	19.40	25.10	21.50	21.80	22.40	14.90	20.40
8	0.39*	0.31*	0.32*	6.00*	0.21*	29.30*	3.82*	0.88*	0.35*	0.27*	0.17*	0.20*
9	34.99*	77.54*	26.43	43.61	22.36*	83.41*	22.28	61.34*	18.26	39.44	29.33*	45.88*
10	6.41	17.30	4.52	15.40	30.40*	11.20	21.00	21.20	*	16.70	26.70	17.80
11	18.00	22.00	43.40	16.60	8.35	18.80	29.60	25.60	15.50	20.00	18.00	21.60
12	11.10	*	19.50	28.40	14.50	32.20*	13.90	11.60	*	6.53	*	8.21
13	19.00	31.00*	151.00*	554.80*	3.27*	8.08*	*	35.80	14.10	12.20	16.00	27.50
14	9.74	15.90	10.70	12.50	10.50	17.50	27.60	17.70	9.44	10.50	9.74	11.20
15	2.00*	6.00*	0.00*	0.00*	5.00*	11.00*	0.00*	0.00*	0.00*	0.00*	10.00	16.00
17	15.50	18.70	16.50	21.50	17.50	18.40	13.90	14.90	19.10	18.00	15.40	16.60
18	139.00*	159.00*	133.00*	175.00*	152.00*	166.00*	169.00*	169.00*	153.00*	166.00*	141.00*	151.00*
19	2.21*	2.49*	1.85*	1.81*	2.40*	3.57*	3.57*	5.72*	1.01*	11.70*	2.21*	3.16*
20	21.10	23.40	22.80	27.00	17.00	18.40	21.30	25.60	21.50	21.30	17.40	18.40
21	224.60*	46.10*	31.20	38.90	58.30*	39.60*	49.50*	43.50*	53.50*	65.50*	80.60*	35.40*
22	19.00	22.20	17.00	16.70	20.00	19.90	24.90	20.50	17.70	31.00	19.80	22.30

TABLE A-18.

ENVIRONMENTAL MONITORING AND SUPPORT LABORATORY
OFFICE OF RESEARCH AND DEVELOPMENT
ENVIRONMENTAL PROTECTION AGENCY

EPA METHOD VALIDATION STUDY-1T ENVIROSCI CHLORCARB

RAW DATA FOR 1,3-DICHLOROBENZENE ANALYSIS BY WATER TYPE
MEDIUM YOUDEN PAIR, UNITS - UG/L

	DISTILLED WATER		TAP WATER		SURFACE WATER		WASTE WATER 1		WASTE WATER 2		WASTE WATER 3	
AMPUL NO:	2	5	2	5	2	5	2	5	2	5	2	5
TRUE CONC:	51.00	59.40	51.00	59.40	51.00	59.40	51.00	59.40	51.00	59.40	51.00	59.40
LAB NUMBER												
1	47.50	44.90	24.80	50.80	39.60	46.80	42.20	63.00	28.40	83.10	42.70	37.30
2	7.92	12.30	16.10	28.10	18.20	37.00	15.10	19.50	25.90	35.60	28.80	11.30
3	32.80	29.90	36.30	32.90	31.90	38.50	30.50	34.70	52.40	69.30	32.70	46.70
4	64.80	58.40	156.00*	221.00*	62.50	105.00*	67.90	47.70	95.70	88.40	84.60*	123.00*
6	39.40	47.00	40.90	48.10	32.90	48.20		74.70	43.40	46.40	37.60	45.00
7	25.80	29.90	56.00	29.40	33.90	48.50	56.40	70.20	27.20	39.20	41.00	47.50
8	0.60*	0.42*	0.42*	2.06*	0.31*	7.61*	0.49*	0.91*	0.31*	5.91*	0.39*	0.66*
9	63.27*	130.48*	93.36	153.42*	105.43*	148.33*	76.32	136.29*	68.43	105.81	164.21*	191.11*
10	5.84	42.40	27.80	33.80	26.40	37.60	37.80	45.40	42.80	27.40	41.40	43.40
11	43.80	51.90	103.00	63.30	38.80	46.80	64.40	69.20	34.00	66.80	49.20	46.40
12	12.80	16.30	25.10	54.70	43.60	43.90	27.00	37.10	13.30	24.20	13.90	29.70
13	49.70	59.80	111.40	34.40	8.27*	2.84*	68.50	262.40*	13.50	15.10	51.70	55.80
14	37.50	42.40	43.90	45.30	43.90	42.60	132.00*	36.80	30.40	48.60	35.40	37.90
15	5.60*	15.00*	34.00*	26.00*	8.10*	10.00*	0.00*	0.00*	5.00*	3.00*	22.00	25.00
17	43.00	45.00	44.00	50.00	22.00	47.00	32.50	41.50	42.00	50.00	44.00	45.00
18	344.00*	363.00*	368.00*	384.00*	361.00*	381.00*	334.00*	402.00*	454.00*	375.00*	369.00*	386.00*
19	4.75*	5.83*	3.88*	5.39*	8.23*	8.18*	7.64*	10.40*	3.32*	9.31*	4.55*	5.71*
20	46.30	49.00	53.80	66.90	40.00	49.40	29.50	33.50	58.90	65.20	40.30	51.20
21	70.00	52.40	96.10	91.40	138.00*	114.50*	161.50*	79.00*	113.80*	115.20*	73.10*	102.90*
22	40.20	31.60	44.50	24.40	41.70	39.10	41.90	34.00	36.80	38.80	34.40	35.10

TABLE A-19.

ENVIRONMENTAL MONITORING AND SUPPORT LABORATORY
OFFICE OF RESEARCH AND DEVELOPMENT
ENVIRONMENTAL PROTECTION AGENCY

EPA METHOD VALIDATION STUDY-IT ENVIROSCI CHTDRCARS

RAW DATA FOR 1,3-DICHLOROBENZENE ANALYSIS BY WATER TYPE
HIGH YOUDEN PAIR, UNITS - UG/L

	DISTILLED WATER		TAP WATER		SURFACE WATER		WASTE WATER 1		WASTE WATER 2		WASTE WATER 3	
AMPUL NO:	3	4	3	4	3	4	3	4	3	4	3	4
TRUE CONC:	204.00	238.00	204.00	238.00	204.00	238.00	204.00	238.00	204.00	238.00	204.00	238.00
LAB NUMBER												
1	120.00	191.00	177.00	199.00	152.00	169.00	162.00	210.00	142.00	165.00	134.00	171.00
2	74.60	83.00	102.00	104.00	125.00	153.00	118.00	91.80	130.00	138.00	76.10	86.10
3	61.30	117.00	107.00	102.00	122.00	135.00	89.60	106.00	89.50	197.00	117.00	116.00
4	309.00	282.00	238.00*	317.00*	135.00	195.00	120.00	95.20	90.30	149.00	163.00	265.00
6	146.00	180.00	166.00	184.00	159.00	197.00	192.00	244.00	164.00	203.00	149.00	180.00
7	157.00	117.00	172.00	204.00	187.00	258.00	235.00	203.00	199.00	233.00	251.00	289.00
8	1.74*	2.38*	1.85*	1.39*	0.55*	1.45*	2.15*	1.86*	1.07*	1.43*	0.68*	2.46*
9	236.75*	288.10*	169.40	198.94	282.06*	263.41*	192.41	208.53	94.39	151.33	251.84*	222.53*
10	64.30	6.92	127.00	120.00	43.00	130.00	162.00	181.00	196.00	120.00	159.00	178.00
11	275.00	300.00	*	266.00	290.00	209.00	236.00	314.00	313.00*	267.00	219.00	295.00
12	100.00	119.00	135.00	154.00	116.00	170.00	111.00	161.00	104.00	137.00	72.30	148.00
13	215.60	252.60	216.80	240.70	47.70*	58.10*	212.60	287.80	67.50	57.30	216.20	219.10
14	157.00	141.00	175.00	197.00	178.00	180.00	174.00	198.00	141.00	161.00	157.00	161.00
15	50.00*	56.00*	0.00*	48.00*	31.00*	52.00*	40.00*	25.00*	39.00*	24.50*	139.00	95.00
17	142.00	175.00	163.00	170.00	160.00	177.00	151.00	203.00	170.00	185.00	88.00	176.00
18	1330.00*	1470.00*	1340.00*	1570.00*	1410.00*	1610.00*	1410.00*	1510.00*	1370.00*	1530.00*	1490.00*	1560.00*
19	23.70*	19.40*	14.20*	21.20*	*	29.70*	33.70*	2.65*	16.20*	18.40*	27.70*	26.90*
20	153.50	225.80	159.90	21.40	158.10	229.10	126.70	228.00	168.20	198.30	144.50	187.40
21	104.00	193.00	252.00	274.60	436.30*	340.20*	326.80*	379.40*	396.00*	342.90*	378.20*	368.30*
22	180.00	201.00	173.40	214.90	175.90	214.70	177.10	219.20	181.50	227.70	180.80	227.00

TABLE A-20.

ENVIRONMENTAL MONITORING AND SUPPORT LABORATORY
OFFICE OF RESEARCH AND DEVELOPMENT
ENVIRONMENTAL PROTECTION AGENCY

EPA METHOD VALIDATION STUDY-IT ENVIROSCI CHLORCARS

RAW DATA FOR 1,4-DICHLOROBENZENE ANALYSIS BY WATER TYPE
LOW YOUDEN PAIR, UNITS - UG/L

	DISTILLED WATER		TAP WATER		SURFACE WATER		WASTE WATER 1		WASTE WATER 2		WASTE WATER 3	
AMPUL NO:	1	6	1	6	1	6	1	6	1	6	1	6
TRUE CONC:	23.00	26.00	23.00	26.00	23.00	26.00	23.00	26.00	23.00	26.00	23.00	26.00
LAB NUMBER												
1	25.90	36.30	30.60	30.90	32.20	23.90	16.60	16.60	21.40	28.50	27.80	22.60
2	13.80	22.80	18.30	21.50	24.60	13.40	4.13	4.92	19.40	24.10	18.60	17.60
3	15.70	16.00	13.70	13.70	13.90	15.70	12.20	14.20	5.27	14.50	18.60	18.90
4	19.90	26.90	70.10*	88.20*	22.60	27.80	23.20	33.90	111.00*	124.00*	54.50*	81.10*
6	19.40	19.30	17.40	18.40	23.30	31.40	*	5.60	22.70	18.40	22.70	15.40
7	15.10	22.50	25.20	20.70	19.00	23.90	28.10	29.90	20.60	25.90	16.60	22.50
8	42.20*	5.20	3.70	425.00*	13.00	54.10	11.30	0.67	7.67*	15.10*	1.04*	3.92*
9	17.38	19.87	15.11	25.49	21.36	36.31	31.41	30.29	21.69	22.55	18.92	48.44*
10	8.24	20.30	5.92	18.90	21.90	13.90	20.30	19.10	*	20.20	19.90	19.90
11	20.00	23.00	41.60	18.50	11.90	20.70	24.00	20.80	17.40	23.20	21.20	25.20
12	54.10*	26.50	35.60	39.30	24.90	40.00	36.90	27.10	25.50	33.10	23.10	33.90*
13	18.70	23.90	*	*	2.95*	5.21*	*	*	17.00	14.90	17.90	21.10
14	5.60	17.20	4.55	5.00	5.80	19.00	0.00*	0.00*	1.35	4.55	2.40*	4.45*
15	4.00*	7.00*	0.00*	0.00*	7.00	11.00	0.00*	5.00*	0.00*	0.00*	12.00	19.00
17	21.70	26.40	23.30	27.50	24.50	26.00	16.20	19.00	27.20	24.90	23.00	24.00
18	202.00*	248.00*	187.00*	278.00*	219.00*	259.00*	223.00*	259.00*	223.00*	259.00*	209.00*	231.00*
19	2.05*	2.24*	1.71*	1.50*	1.99*	2.75*	1.39*	3.23*	0.84*	4.93*	1.80*	2.28*
20	26.20	36.70	26.40	33.50	28.40	32.00	22.30	26.20	16.90	37.60	19.50	20.30
21	121.90*	31.30	31.20	51.80	43.50	27.70	26.10	33.50	38.90	56.90*	42.50*	25.80
22	21.50	24.30	18.50	13.90	22.20	21.10	23.00	26.90	18.90	35.60	22.00	22.90

TABLE A-21.

ENVIRONMENTAL MONITORING AND SUPPORT LABORATORY
OFFICE OF RESEARCH AND DEVELOPMENT
ENVIRONMENTAL PROTECTION AGENCY

EPA METHOD VALIDATION STUDY-1T ENVIROSCI CHTDRCARS

RAW DATA FOR 1,4-DICHLOROBENZENE ANALYSIS BY WATER TYPE
MEDIUM YOUDEN PAIR, UNITS - UG/L

	DISTILLED WATER		TAP WATER		SURFACE WATER		WASTE WATER 1		WASTE WATER 2		WASTE WATER 3	
AMPUL NO:	2	5	2	5	2	5	2	5	2	5	2	5
TRUE CONC:	172.00	194.00	172.00	194.00	172.00	194.00	172.00	194.00	172.00	194.00	172.00	194.00
LAB NUMBER												
1	167.00	155.00	85.00	176.00	127.00	163.00	92.90	195.00	105.00	180.00	151.00	135.00
2	152.00	188.00	132.00	175.00	224.00	238.00	136.00	147.00	163.00	225.00	180.00	168.00
3	82.90	98.30	102.00	47.90	94.50	106.00	116.00	96.90	106.00	128.00	57.40	89.70
4	117.00	129.00	340.00+	366.00+	131.00	194.00	192.00	117.00	192.00	218.00	194.00+	370.00+
6	120.00	137.00	128.00	142.00	137.00	168.00	143.00	134.00	156.00	169.00	137.00	161.00
7	91.60	99.00	176.00	99.20	116.00	160.00	155.00	201.00	98.70	149.00	141.00	156.00
8	85.60	56.50	27.00	233.00	35.50	40.90	43.20	178.00	40.10+	36.60+	55.30+	5.62+
9	124.90	155.50	108.40	136.45	86.25	108.73	92.39	126.44	72.53	111.88	177.08	155.52
10	19.80+	140.00	94.60	120.00	149.00	125.00	118.00	146.00	182.00	94.60	153.00	158.00
11	160.00	188.00	202.00	185.00	134.00	151.00	176.00	186.00	116.00	262.00	175.00	203.00
12	137.00	146.00	127.00	160.00	145.00	156.00	125.00	146.00	112.00	140.00	124.00	157.00
13	169.00	221.10	272.80+	+	23.20+	10.10+	212.80+	+	47.70	53.20	163.60	190.80
14	155.00	154.00	172.00	160.00	175.00	171.00	156.00	121.00	120.00	181.00	152.00	146.00
15	33.00+	83.00+	111.00+	65.00+	44.00	59.00	30.00+	88.00+	29.00+	24.50+	96.00	104.00
17	157.00	175.00	175.00	193.00	35.00	183.00	147.00	180.00	173.00	194.00	17.70	185.00
18	1440.00+	1580.00+	1530.00+	1580.00+	1500.00+	1660.00+	1680.00+	1670.00+	1680.00+	1670.00+	1530.00+	1680.00+
19	10.90+	12.80+	8.80+	11.80+	18.10+	18.30+	12.10+	16.20+	5.91+	16.20+	10.17+	12.60+
20	140.50	210.30	187.90	218.20	169.00	184.00	143.30	171.80	187.20	225.80	149.60	178.50
21	128.50	100.80	194.40	185.80	263.50	216.00	235.00	125.50	204.60	208.70	137.80	195.30
22	128.60	97.30	137.90	100.70	131.70	107.40	128.80	75.90	105.60	102.80	105.60	106.70

TABLE A-22.

ENVIRONMENTAL MONITORING AND SUPPORT LABORATORY
OFFICE OF RESEARCH AND DEVELOPMENT
ENVIRONMENTAL PROTECTION AGENCY

EPA METHOD VALIDATION STUDY-IT ENVIROSCI CHTDRCARS

RAW DATA FOR 1,4-DICHLOROBENZENE ANALYSIS BY WATER TYPE
HIGH YOUDEN PAIR. UNITS - UG/L

	DISTILLED WATER		TAP WATER		SURFACE WATER		WASTE WATER 1		WASTE WATER 2		WASTE WATER 3	
AMPUL NO:	3	4	3	4	3	4	3	4	3	4	3	4
TRUE CONC:	288.00	324.00	288.00	324.00	288.00	324.00	288.00	324.00	288.00	324.00	288.00	324.00
LAB NUMBER												
1	186.00	261.00	268.00	264.00	229.00	245.00	260.00	319.00	222.00	253.00	231.00	277.00
2	153.00	238.00	176.00	194.00	287.00	337.00	204.00	168.00	235.00	251.00	190.00	159.00
3	87.40	160.00	154.00	143.00	170.00	183.00	132.00	140.00	114.00	212.00	145.00	144.00
4	409.00	396.00	275.00+	340.00+	156.00	200.00	186.00	133.00	118.00	204.00	243.00+	365.00+
6	193.00	233.00	221.00	240.00	253.00	299.00	225.00	262.00	251.00	312.00	243.00	264.00
7	258.00	193.00	261.00	320.00	301.00	387.00	362.00	313.00	319.00	372.00	401.00	451.00
8	105.00	93.50	66.80	177.00	48.40	21.00	375.00	229.00	100.00+	9.13+	56.90+	38.30+
9	165.43	164.31	159.04	182.59	142.36	157.59	142.81	181.65	106.41	123.63	208.32	171.64
10	91.00	8.39	194.00	172.00	45.00	205.00	202.00	233.00	264.00	165.00	223.00	240.00
11	341.00	356.00	+	297.00	368.00	266.00	261.00	360.00	398.00	327.00	273.00	377.00
12	199.00	214.00	215.00	246.00	185.00	244.00	191.00	248.00	193.00	218.00	149.00	247.00
13	265.30	314.60	245.60+	305.00+	59.30+	77.40+	277.90+	298.20+	95.00	87.90	299.30	304.20
14	244.00	206.00	233.00	287.00	266.00	271.00	230.00	250.00	218.00	200.00	239.00	236.00
15	87.00+	85.00+	28.00+	28.00+	52.00	72.00	90.00+	64.00+	44.50+	43.50+	167.00	125.00
17	250.00	301.00	293.00	300.00	280.00	300.00	274.00	340.00	288.00	320.00	26.60	310.00
18	2450.00+	2450.00+	2480.00+	2610.00+	2400.00+	2680.00+	2340.00+	2520.00+	2340.00+	2520.00+	2540.00+	2590.00+
19	24.80+	20.10+	14.50+	21.90+	+	28.80+	28.20+	1.01+	12.30+	13.60+	24.40+	25.50+
20	162.60	270.30	199.80	248.60	207.30	281.30	240.20	216.10	237.00	255.40	177.60	224.50
21	100.50	175.00	235.40	249.50	383.30	297.70	263.00	287.10	336.60	265.20	324.30	309.50
22	246.80	272.00	233.00	283.90	243.20	283.00	250.20	281.00	259.70	285.70	247.30	292.70

TABLE A-23.

ENVIRONMENTAL MONITORING AND SUPPORT LABORATORY
OFFICE OF RESEARCH AND DEVELOPMENT
ENVIRONMENTAL PROTECTION AGENCY

EPA METHOD VALIDATION STUDY-1T ENVIROSCI CHLORCARS

RAW DATA FOR 1,2,4-TRICHLOROBENZENE ANALYSIS BY WATER TYPE
LOW YOUDEN PAIR, UNITS - UG/L

	DISTILLED WATER		TAP WATER		SURFACE WATER		WASTE WATER 1		WASTE WATER 2		WASTE WATER 3	
AMPUL NO:	1	6	1	6	1	6	1	6	1	6	1	6
TRUE CONC:	15.10	17.30	15.10	17.30	15.10	17.30	15.10	17.30	15.10	17.30	15.10	17.30
LAB NUMBER												
1	11.40	14.70	12.90	17.80	9.14	14.80	11.70	16.60	10.60	14.80	14.30	13.10
2	8.56	14.10	10.40	11.60	13.30	11.90	7.98	9.57	12.60	14.10	8.83	12.00
3	8.60	9.50	7.45	8.00	7.90	8.95	8.65	9.00	2.15	10.30	6.70+	7.20+
4	11.10	29.30+	92.00+	65.60+	24.80	31.20	18.10	66.10+	55.70+	130.00+	45.60+	61.60+
6	15.40	17.50	14.20	16.10	14.40	18.20	14.00	14.80	16.80	17.10	16.50	20.70
7	8.01	10.70	12.20	12.70	11.40	12.80	12.00	11.90	10.30	14.70	11.20	13.00
8	0.00+	6.65+	4.51	73.30+	3.14	98.00+	48.50+	2.51	5.37+	4.01+	66.60+	4.62
9	14.64	8.16	11.88	6.93	9.97	5.96	8.44	18.55	6.67	7.18	25.37	12.12
10	5.77	12.20	4.22	11.70	12.10	7.50	9.08	11.00	*	12.20	12.30	11.90
11	9.89	14.10	9.19	9.33	4.50	9.77	9.50	6.40	9.67	10.80	10.00	14.80
12	13.30	18.70	14.00	16.90	17.10	17.80	12.60	16.10	14.30	18.40	16.00	17.70
13	12.40	14.20	12.10	12.30	2.18+	3.72+	7.93	12.90	10.20+	4.90+	11.10	13.20
14	73.10+	36.20+	66.40+	80.30+	6.75	84.80+	67.20+	82.90+	10.30	67.40+	34.00+	20.50+
15	1.20+	4.30+	2.80+	5.40+	4.30+	7.00+	3.10+	4.00+	0.75+	0.75+	6.00+	9.00+
17	11.30	12.90	12.24	15.00	12.60	13.90	11.40	13.10	12.90	14.40	11.40	12.10
18	114.00+	151.00+	107.00+	161.00+	121.00+	185.00+	120.00+	156.00+	120.00+	156.00+	121.00+	140.00+
19	16.10	16.50	14.00	17.30	18.10	26.70	17.70	19.50	5.45	13.30	17.80	18.40
20	19.30	19.00	17.30	19.90	18.10	17.00	14.80	18.40	15.50	20.40	16.50	17.80
21	28.80+	50.20+	32.50+	27.70	56.30+	39.40+	34.90+	39.90+	43.60+	24.50+	43.20+	47.00+
22	16.20	16.70	14.70	16.00	16.90	14.90	17.60	10.40	14.60	15.90	17.00	16.90

TABLE A-24.

ENVIRONMENTAL MONITORING AND SUPPORT LABORATORY
OFFICE OF RESEARCH AND DEVELOPMENT
ENVIRONMENTAL PROTECTION AGENCY

EPA METHOD VALIDATION STUDY-IT ENVIROSCI CHTDRCARS

RAW DATA FOR 1,2,4-TRICHLOROBENZENE ANALYSIS BY WATER TYPE
MEDIUM YOUDEN PAIR, UNITS - UG/L

	DISTILLED WATER		TAP WATER		SURFACE WATER		WASTE WATER 1		WASTE WATER 2		WASTE WATER 3	
AMPUL NO:	2	5	2	5	2	5	2	5	2	5	2	5
TRUE CONC:	37.80	43.20	37.80	43.20	37.80	43.20	37.80	43.20	37.80	43.20	37.80	43.20
LAB NUMBER												
1	39.90	37.80	20.90	42.00	34.10	40.50	23.70	43.40	24.90	70.20	35.70	33.70
2	19.00	24.20	17.20	23.10	24.10	25.30	18.30	21.00	20.30	25.80	20.80	22.50
3	20.20	25.50	22.00	24.50	20.00	23.00	13.00	24.50	22.00	28.00	9.00+	12.50+
4	54.30	142.00+	346.00+	117.00+	69.40	146.00+	87.60+	52.20	113.00+	142.00+	30.10	175.00+
6	37.90	41.70	37.60	43.30	44.30	53.30	39.00	42.40	46.60	52.40	48.10	57.60
7	20.20	21.20	39.90	21.70	26.00	36.60	28.80	38.00	28.40	32.50	30.20	34.80
8	7.93+	4.51+	5.88	14.40	10.70	27.50	5.38	45.20	7.05+	23.40+	5.44+	27.20
9	35.29	67.93	26.51	41.82	22.37	54.66	32.39	79.66	17.68	61.67	32.74	83.90
10	4.76	31.40	21.60	23.40	24.80	31.10	23.20	26.80	27.40	19.90	24.20	28.60
11	26.30	34.30	23.30	30.20	19.00	25.30	27.20	26.40	19.70	46.70	29.20	36.00
12	34.50	36.50	35.40	40.20	54.00	41.40	31.90	37.70	30.50	38.80	34.00	40.80
13	33.30	21.80	23.40	20.60	4.41+	2.62+	37.50	33.50	9.54+	12.90+	21.50	21.80
14	193.00+	188.00+	57.50+	215.00+	75.60	113.00+	191.00+	215.00+	178.00+	265.00+	191.00+	180.00+
15	4.70+	9.10+	5.80+	5.00+	6.90+	5.90+	5.30+	9.00+	1.35+	1.20+	8.60+	15.00+
17	29.30	32.50	31.70	37.50	15.70	34.10	29.90	34.20	33.20	35.70	32.20	33.20
18	307.00+	356.00+	328.00+	362.00+	323.00+	366.00+	338.00+	362.00+	338.00+	360.00+	327.00+	385.00+
19	14.00	50.50	31.30	41.10	63.30	67.70	48.70	81.90	23.30	70.70	35.80	66.10
20	41.10	44.90	43.20	54.70	39.10	45.80	31.10	36.30	43.40	54.90	38.10	45.10
21	82.50+	58.80	103.70+	99.00+	151.11+	118.80+	159.90+	205.60+	110.70+	119.90+	84.80+	115.30+
22	37.60	26.20	41.40	14.50	38.80	29.70	30.60	28.00	30.30	30.90	31.30	28.10

TABLE A-25.

ENVIRONMENTAL MONITORING AND SUPPORT LABORATORY
OFFICE OF RESEARCH AND DEVELOPMENT
ENVIRONMENTAL PROTECTION AGENCY

EPA METHOD VALIDATION STUDY-IT ENVIROSCI CHTDRCARS

RAW DATA FOR 1,2,4-TRICHLOROBENZENE ANALYSIS BY WATER TYPE
HIGH YOUDEN PAIR, UNITS - UG/L

	DISTILLED WATER		TAP WATER		SURFACE WATER		WASTE WATER 1		WASTE WATER 2		WASTE WATER 3	
AMPUL NO:	3	4	3	4	3	4	3	4	3	4	3	4
TRUE CONC:	188.00	216.00	188.00	216.00	188.00	216.00	188.00	216.00	188.00	216.00	188.00	216.00
LAB NUMBER												
1	112.00	187.00	176.00	192.00	164.00	181.00	140.00	197.00	168.00	176.00	128.00	174.00
2	98.80	135.00	113.00	111.00	141.00	167.00	119.00	110.00	122.00	134.00	116.00	120.00
3	69.00	104.00	97.50	92.50	104.00	126.00	84.00	93.50	67.00	120.00	81.50+	84.50+
4	383.00+	368.00	256.00+	403.00+	204.00	186.00	145.00	227.00	132.00	234.00	222.00	454.00+
6	145.00	182.00	162.00	176.00	174.00	215.00	188.00	223.00	186.00	221.00	182.00	215.00
7	128.00	97.00	132.00	162.00	152.00	177.00	182.00	160.00	161.00	199.00	198.00	228.00
8	10.70+	9.38+	9.33+	28.60	5.22	30.60	41.10	30.00	9.59+	46.80+	0.00+	39.70
9	171.22	171.45	108.94	120.38	63.81	82.93	91.82	83.41	63.58	82.92	48.51	64.23
10	60.90	4.51	107.00	96.00	34.20	108.00	139.00	150.00	122.00	105.00	135.00	149.00
11	176.00	189.00	*	103.00	179.00	137.00	152.00	186.00	215.00	178.00	159.00	200.00
12	126.00	138.00	137.00	158.00	120.00	149.00	121.00	167.00	133.00	143.00	99.30	173.00
13	120.10	148.50	102.70	123.00	45.30+	49.00+	107.50	124.10	48.60+	48.40+	127.50	131.30
14	1192.00+	901.00+	1220.00+	689.00+	1150.00+	1330.00+	1026.00+	679.00+	1000.00+	758.00+	1160.00+	1110.00+
15	47.10+	53.00+	36.00+	40.00+	31.70+	41.30+	67.00+	50.00+	7.00+	7.00+	83.00+	62.00+
17	138.00	161.00	139.00	152.00	143.00	152.00	145.00	212.00	152.00	167.00	137.00	160.00
18	1390.00+	2170.00+	1410.00+	2340.00+	2120.00+	2400.00+	2050.00+	2310.00+	2050.00+	2310.00+	2260.00+	1630.00+
19	148.00	176.00	152.00	184.00	*	28.10	266.00	14.30	110.00	113.00	175.00	211.00
20	160.80	197.90	150.70	192.50	156.50	205.30	141.90	147.60	150.10	180.80	151.50	186.70
21	165.00	260.30	916.40+	356.40+	564.80+	438.50+	480.90+	481.80+	330.00+	294.50+	505.00+	537.60+
22	169.10	193.60	162.60	194.70	164.90	198.60	159.10	193.20	182.40	179.60	172.90	185.00

TABLE A-26.

ENVIRONMENTAL MONITORING AND SUPPORT LABORATORY
OFFICE OF RESEARCH AND DEVELOPMENT
ENVIRONMENTAL PROTECTION AGENCY

EPA METHOD VALIDATION STUDY-IT ENVIROSCI CHTDRCARS

RAW DATA FOR HEXACHLOROBENZENE ANALYSIS BY WATER TYPE
LOW YOUDEN PAIR, UNITS - UG/L

	DISTILLED WATER		TAP WATER		SURFACE WATER		WASTE WATER 1		WASTE WATER 2		WASTE WATER 3	
AMPUL NO:	1	6	1	6	1	6	1	6	1	6	1	6
TRUE CONC:	1.49	1.29	1.49	1.29	1.49	1.29	1.49	1.29	1.49	1.29	1.49	1.29
LAB NUMBER												
1	1.24	1.28	1.43	1.29	1.41	1.27	1.30	1.30	1.16	1.30	1.55	1.22
2	0.80	1.20	1.16	1.07	1.44	1.28	1.34	1.15	1.41	1.27	1.30	1.11
3	1.68	0.78	0.86	0.72	1.01	0.94	0.95	3.75+	0.88	0.91	0.74	0.62
4	12.50+	12.50+	19.40+	11.70+	12.70+	11.60+	18.40+	19.50+	16.30+	12.70+	11.70+	13.20+
6	1.42	1.20	1.37	1.19	1.84	1.08	1.42	1.05	1.35	1.05	1.47	1.47
7	0.76	1.00	1.58	1.11	1.18	0.94	1.24	1.04	1.08	1.14	1.09	1.03
8	1.16	0.94	0.95	0.85	1.16	0.98	0.86	1.13	0.16	0.89	0.34	0.78
9	1.38	1.90+	1.41	0.96	2.01	1.38	3.08+	2.74	1.62	1.84	3.75+	2.25
10	0.77	1.20	0.70	1.28	1.30	0.93	1.19	1.09	*	1.32	1.22	1.14
11	1.21	0.87	1.16	1.04	0.60	0.93	1.04	2.00	1.53	1.16	1.60	2.40
12	1.29	1.18	1.55	1.28	1.66	1.18	1.94	1.18	1.32	1.15	1.40	1.23
13	0.07+	0.21+	1.50	1.17	*	0.03+	3.80+	1.28	0.61+	0.22+	0.03+	0.08+
14	3.70+	3.70+	3.71+	3.26+	4.13+	3.53+	4.10+	3.47+	3.22	3.19	4.47+	4.10+
15	0.10+	0.10+	0.10+	0.13+	0.04+	0.12+	0.05+	0.04+	0.16+	0.09+	0.06+	0.07+
17	0.99	0.80	1.05	1.00	1.15	1.00	1.15	0.64	1.21	0.98	0.54	0.50
18	8.61+	5.40+	7.05+	4.70+	8.54+	3.87+	0.11+	6.70+	14.80+	14.90+	0.29	0.00+
19	1.41	1.27	1.14	0.97	1.45	1.46	1.32	1.31	6.76+	1.06	0.74	1.37
20	1.50	1.40	1.38	1.33	1.60	1.40	1.50	1.50	1.30	1.40	1.20	1.30
21	1.40	1.40	1.70	1.40	2.30	1.30	1.50	2.30	2.80	2.90	1.40	1.70
22	1.42	1.22	1.47	1.30	1.44	1.27	1.56	1.25	1.30	1.45	1.50	1.33

TABLE A-27.

ENVIRONMENTAL MONITORING AND SUPPORT LABORATORY
OFFICE OF RESEARCH AND DEVELOPMENT
ENVIRONMENTAL PROTECTION AGENCY

EPA METHOD VALIDATION STUDY-IT ENVIROSCI CHTDRCARS

RAW DATA FOR HEXACHLOROBENZENE ANALYSIS BY WATER TYPE
MEDIUM YOUDEN PAIR, UNITS - UG/L

	DISTILLED WATER		TAP WATER		SURFACE WATER		WASTE WATER 1		WASTE WATER 2		WASTE WATER 3	
AMPUL NO:	2	5	2	5	2	5	2	5	2	5	2	5
TRUE CONC:	7.44	6.46	7.44	6.46	7.44	6.46	7.44	6.46	7.44	6.46	7.44	6.46
LAB NUMBER												
1	6.98	6.94	6.71	7.11	7.03	6.76	5.13	6.52	5.61	6.45	7.29	6.45
2	4.94	5.46	4.85	5.16	6.78	6.31	6.36	5.73	5.49	6.11	6.35	5.47
3	4.95	4.30	4.95	5.55	4.65	4.90	5.50	4.80	5.70	4.40	2.27	1.67
4	60.20+	73.70+	75.70+	63.30+	72.10+	105.00+	76.90+	41.50+	53.40+	65.40+	50.60+	47.40+
6	7.14	6.46	7.16	5.73	7.61	6.05	8.42	7.40	7.56	7.06	7.79	6.34
7	7.19	6.85	9.48	6.83	7.13	8.62	8.35	7.91	10.50	8.35	8.67	7.84
8	3.03	2.72	2.64	10.20	4.36	18.90+	2.01	5.57	0.60	1.25	3.15	0.86
9	6.36	10.30	4.03	8.43	7.88	8.52	5.53	14.64+	6.12	11.30	5.96	11.43
10	2.04	5.35	6.06	5.72	6.26	5.52	6.06	6.50	6.54	4.44	4.59	6.53
11	9.20	7.57	1.62	6.26	5.01	6.62	7.44	7.20	24.00+	9.14	8.80	6.80
12	6.27	5.31	5.48	5.45	6.39	5.56	5.76	5.74	5.16	5.20	6.25	5.21
13	1.91+	1.88+	7.05	7.17	0.11+	0.12+	4.86	6.54	1.24+	1.15+	0.57+	0.48+
14	18.10+	15.40+	17.60+	15.20+	18.80+	17.00+	19.40+	16.80+	17.90+	17.10	17.70+	14.70+
15	0.80+	0.60+	0.77+	0.79+	0.85+	0.79+	0.68+	0.82+	0.72+	0.52+	0.36+	0.39+
17	5.90	5.30	5.40	5.00	6.20	5.00	5.80	3.90	6.00	5.30	5.00	4.90
18	59.20+	47.00+	51.00+	22.60+	39.10+	48.80+	61.00+	30.00+	68.30+	58.60+	26.80+	1.19
19	5.73	5.80	2.83	2.83	5.26	6.07	5.60	5.33	5.14	4.00	3.61	4.43
20	6.90	6.50	6.79	6.60	6.90	7.10	7.20	7.20	6.80	6.30	6.70	5.90
21	8.10	7.10	7.80	6.80	12.00+	11.30+	6.20	6.20	12.00	11.10	7.80	9.00
22	6.74	5.00	6.79	6.79	6.48	6.79	6.23	5.78	6.20	8.58	6.61	5.33

TABLE A-28.

ENVIRONMENTAL MONITORING AND SUPPORT LABORATORY
OFFICE OF RESEARCH AND DEVELOPMENT
ENVIRONMENTAL PROTECTION AGENCY

EPA METHOD VALIDATION STUDY-IT ENVIROSCI CHTDRCARS

RAW DATA FOR HEXACHLOROBENZENE ANALYSIS BY WATER TYPE
HIGH YOUDEN PAIR, UNITS - UG/L

	DISTILLED WATER		TAP WATER		SURFACE WATER		WASTE WATER 1		WASTE WATER 2		WASTE WATER 3	
AMPUL NO:	3	4	3	4	3	4	3	4	3	4	3	4
TRUE CONC:	14.90	12.90	14.90	12.90	14.90	12.90	14.90	12.90	14.90	12.90	14.90	12.90
LAB NUMBER												
1	14.40	14.50	14.60	14.10	13.40	14.70	14.40	13.00	15.00	13.90	14.90	13.70
2	9.48	10.80	11.40	10.70	13.80	12.20	12.00	10.80	13.30	12.20	12.20	9.49
3	8.85	7.90	10.40	8.40	11.20	10.60	11.90	9.25	7.90	11.20	9.17	7.07
4	135.00+	104.00+	142.00+	119.00+	121.00+	115.00+	98.50+	88.80+	97.60+	92.20+	83.20+	98.40+
6	19.20	15.70	19.50	15.60	18.80	18.70	14.40	12.10	20.50	20.10+	15.00	19.40
7	15.90	12.80	15.40	18.40	17.10	15.70	18.80	14.30	11.50	11.90	11.80	16.10
8	4.92	0.54	39.50+	24.10	24.70	24.00+	41.70+	11.00	39.50	35.40+	4.49	4.73
9	18.23	16.07	11.21	14.73	13.21	14.64	12.35	15.81	9.91	10.84	7.99	9.69
10	7.00	1.19	11.90	10.90	11.60	10.90	11.50	11.50	11.90	10.80	13.60	11.70
11	18.80	16.70	*	7.31	12.40	9.22	18.00	14.00	18.40	13.70	19.10	15.20
12	10.80	9.86	11.60	9.56	10.70	10.30	10.50	10.80	11.00	9.54	8.35	12.20
13	5.82+	5.87+	13.90	12.70	0.93+	0.82+	10.90	8.62	4.36+	4.03+	1.34+	1.15+
14	16.40+	22.90+	32.50+	30.10+	35.20+	31.60+	32.50+	27.40+	32.40	13.50	32.10+	28.70+
15	1.60+	1.60+	1.51+	1.17+	1.46+	1.39+	4.22+	1.62+	1.95+	0.98+	1.65+	0.66+
17	11.30	11.50	10.70	9.90	11.40	10.00	11.10	9.90	11.00	12.00	10.00	10.00
18	57.20+	90.80+	50.80+	74.50+	105.00+	88.00+	98.50+	82.20+	117.00+	104.00+	42.60+	82.10+
19	13.30	12.60	12.10	6.83	*	11.30	12.00	8.20	10.60	9.30	5.21	6.11
20	13.70	11.70	12.60	12.30	14.30	12.70	13.50	11.80	11.30	11.10	11.50	14.00
21	13.20	12.20	18.70	19.40	21.30	16.80	16.20	11.80	22.00	16.40	21.10	11.00
22	12.20	12.60	12.80	12.00	12.80	12.10	12.10	11.80	13.40	11.70	12.90	12.70

TABLE A-29.

ENVIRONMENTAL MONITORING AND SUPPORT LABORATORY
OFFICE OF RESEARCH AND DEVELOPMENT
ENVIRONMENTAL PROTECTION AGENCY

EPA METHOD VALIDATION STUDY-IT ENVIROSCI CHLORCARS

EFFECT OF WATER TYPE ON HEXACHLOROETHANE ANALYSIS

** POINT ESTIMATES **

DISTILLED WATER SLOPE:GAMMA(1) = .96777

WATER	INTERCEPT(WATER-DISTILLED)	SLOPE(WATER-DISTILLED)
2	-.0202	.0678
3	.1113	.0099
4	.1743	-.0085
5	-.0225	.0046
6	.0580	.0686

** ANALYSIS OF VARIANCE **

SOURCE	DF	SUM OF SQUARES	MEAN SQUARE	F	PROB
REG(DISTILLED)	1	581.02090	581.02090		
REG(WATER/DISTILLED)	10	3.13687	.31369	1.91	.0413
ERROR	511	83.84065	.16407		
TOTAL	522	667.99842			

** TABLE OF 95% CONFIDENCE INTERVALS FOR THE DIFFERENCES BETWEEN INTERCEPTS AND THE DIFFERENCES BETWEEN SLOPES **

WATER	INTERCEPT(WATER-DISTILLED) ESTIMATE	INTERVAL	SLOPE(WATER-DISTILLED) ESTIMATE	INTERVAL
2	-.0202	(-.2896 , .2492)	.0678	(-.0959 , .2315)
3	.1113	(-.1510 , .3737)	.0099	(-.1504 , .1702)
4	.1743	(-.0898 , .4384)	-.0085	(-.1705 , .1535)
5	-.0225	(-.2890 , .2440)	.0046	(-.1567 , .1660)
6	.0580	(-.2177 , .3337)	.0686	(-.0998 , .2371)

NOTE: IF ZERO IS CONTAINED WITHIN A GIVEN CONFIDENCE INTERVAL THEN THERE IS NO STATISTICAL SIGNIFICANCE BETWEEN DISTILLED WATER AND THE CORRESPONDING WASTE WATER FOR THE ASSOCIATED PARAMETER(INTERCEPT/SLOPE).

THE SLOPE AND INTERCEPT ESTIMATES FROM THIS ANALYSIS ARE NOT THE SAME AS THOSE OBTAINED FROM THE PRECISION AND ACCURACY REGRESSIONS PERFORMED EARLIER.

TABLE A-30.

ENVIRONMENTAL MONITORING AND SUPPORT LABORATORY
OFFICE OF RESEARCH AND DEVELOPMENT
ENVIRONMENTAL PROTECTION AGENCY

EPA METHOD VALIDATION STUDY-1T ENVIROSCI CHLORCARS

EFFECT OF WATER TYPE ON HEXACHLOROBUTADIENE ANALYSIS

** POINT ESTIMATES **

DISTILLED WATER SLOPE:GAMMA(1) = .95687

WATER	INTERCEPT(WATER-DISTILLED)	SLOPE(WATER-DISTILLED)
2	.0587	.0149
3	.1441	.0136
4	.1395	.0089
5	.1569	.0077
6	.2693	-.0013

** ANALYSIS OF VARIANCE **

SOURCE	DF	SUM OF SQUARES	MEAN SQUARE	F	PROB
REG(DISTILLED)	1	520.11079	520.11079		
REG(WATER/DISTILLED)	10	3.73582	.37358	1.98	.0330
ERROR	502	94.48044	.18821		
TOTAL	513	618.32705			

** TABLE OF 95% CONFIDENCE INTERVALS FOR THE DIFFERENCES BETWEEN INTERCEPTS AND THE DIFFERENCES BETWEEN SLOPES **

WATER	INTERCEPT(WATER-DISTILLED) ESTIMATE	INTERCEPT(WATER-DISTILLED) INTERVAL	SLOPE(WATER-DISTILLED) ESTIMATE	SLOPE(WATER-DISTILLED) INTERVAL
2	.0587	(-.4464 , .5637)	.0149	(-.1607 , .1905)
3	.1441	(-.3707 , .6589)	.0136	(-.1657 , .1929)
4	.1395	(-.3609 , .6400)	.0089	(-.1655 , .1834)
5	.1569	(-.3627 , .6764)	.0077	(-.1722 , .1876)
6	.2693	(-.2262 , .7649)	-.0013	(-.1737 , .1710)

NOTE: IF ZERO IS CONTAINED WITHIN A GIVEN CONFIDENCE INTERVAL THEN THERE IS NO STATISTICAL SIGNIFICANCE BETWEEN DISTILLED WATER AND THE CORRESPONDING WASTE WATER FOR THE ASSOCIATED PARAMETER(INTERCEPT/SLOPE).

THE SLOPE AND INTERCEPT ESTIMATES FROM THIS ANALYSIS ARE NOT THE SAME AS THOSE OBTAINED FROM THE PRECISION AND ACCURACY REGRESSIONS PERFORMED EARLIER.

TABLE A-31.

ENVIRONMENTAL MONITORING AND SUPPORT LABORATORY
OFFICE OF RESEARCH AND DEVELOPMENT
ENVIRONMENTAL PROTECTION AGENCY

EPA METHOD VALIDATION STUDY-IT ENVIROSCI CHTDRCARS

EFFECT OF WATER TYPE ON 2-CHLORONAPHTHALENE ANALYSIS

** POINT ESTIMATES **

DISTILLED WATER SLOPE:GAMMA(1) = .92294

WATER	INTERCEPT(WATER-DISTILLED)	SLOPE(WATER-DISTILLED)
2	.0717	.0004
3	.0809	.0070
4	.5307	-.0760
5	.3396	-.0531
6	-.2654	.0585

** ANALYSIS OF VARIANCE **

SOURCE	DF	SUM OF SQUARES	MEAN SQUARE	F	PROB
REG(DISTILLED)	1	586.29807	586.29807		
REG(WATER/DISTILLED)	10	4.04280	.40428	3.12	.0007
ERROR	571	73.99842	.12959		
TOTAL	582	664.33930			

** TABLE OF 95% CONFIDENCE INTERVALS FOR THE DIFFERENCES BETWEEN INTERCEPTS AND THE DIFFERENCES BETWEEN SLOPES **

WATER	INTERCEPT(WATER-DISTILLED) ESTIMATE	INTERVAL	SLOPE(WATER-DISTILLED) ESTIMATE	INTERVAL
2	.0717	(-.5534 , .6967)	.0004	(-.1330 , .1338)
3	.0809	(-.5393 , .7011)	.0070	(-.1257 , .1398)
4	.5307	(-.0671 , 1.1284)	-.0760	(-.2038 , .0518)
5	.3396	(-.2794 , .9587)	-.0531	(-.1852 , .0790)
6	-.2654	(-.8702 , .3395)	.0585	(-.0705 , .1875)

NOTE: IF ZERO IS CONTAINED WITHIN A GIVEN CONFIDENCE INTERVAL THEN THERE IS NO STATISTICAL SIGNIFICANCE BETWEEN DISTILLED WATER AND THE CORRESPONDING WASTE WATER FOR THE ASSOCIATED PARAMETER(INTERCEPT/SLOPE).

THE SLOPE AND INTERCEPT ESTIMATES FROM THIS ANALYSIS ARE NOT THE SAME AS THOSE OBTAINED FROM THE PRECISION AND ACCURACY REGRESSIONS PERFORMED EARLIER.

TABLE A-32.

ENVIRONMENTAL MONITORING AND SUPPORT LABORATORY
OFFICE OF RESEARCH AND DEVELOPMENT
ENVIRONMENTAL PROTECTION AGENCY

EPA METHOD VALIDATION STUDY-IT ENVIROSCI CHTDRCARS

EFFECT OF WATER TYPE ON 1,2-DICHLOROBENZENE ANALYSIS

** POINT ESTIMATES **

DISTILLED WATER SLOPE:GAMMA(1) = .94194

WATER	INTERCEPT(WATER-DISTILLED)	SLOPE(WATER-DISTILLED)
2	.2175	-.0131
3	-.1951	.0454
4	-.3984	.0906
5	.0493	.0004
6	.2306	-.0179

** ANALYSIS OF VARIANCE **

SOURCE	DF	SUM OF SQUARES	MEAN SQUARE	F	PROB
REG(DISTILLED)	1	464.05882	464.05882		
REG(WATER/DISTILLED)	10	2.71826	.27183	2.38	.0092
ERROR	521	59.48722	.11418		
TOTAL	532	526.26429			

** TABLE OF 95% CONFIDENCE INTERVALS FOR THE DIFFERENCES BETWEEN INTERCEPTS AND THE DIFFERENCES BETWEEN SLOPES **

WATER	INTERCEPT(WATER-DISTILLED) ESTIMATE	INTERVAL	SLOPE(WATER-DISTILLED) ESTIMATE	INTERVAL
2	.2175	(-.4837 , .9187)	-.0131	(-.1566 , .1303)
3	-.1951	(-.9280 , .5377)	.0454	(-.1038 , .1946)
4	-.3984	(-1.0975 , .3007)	.0906	(-.0521 , .2334)
5	.0493	(-.6827 , .7812)	.0004	(-.1481 , .1490)
6	.2306	(-.4794 , .9405)	-.0179	(-.1623 , .1265)

NOTE: IF ZERO IS CONTAINED WITHIN A GIVEN CONFIDENCE INTERVAL THEN THERE IS NO STATISTICAL SIGNIFICANCE BETWEEN DISTILLED WATER AND THE CORRESPONDING WASTE WATER FOR THE ASSOCIATED PARAMETER(INTERCEPT/SLOPE).

THE SLOPE AND INTERCEPT ESTIMATES FROM THIS ANALYSIS ARE NOT THE SAME AS THOSE OBTAINED FROM THE PRECISION AND ACCURACY REGRESSIONS PERFORMED EARLIER.

TABLE A-33.

ENVIRONMENTAL MONITORING AND SUPPORT LABORATORY
OFFICE OF RESEARCH AND DEVELOPMENT
ENVIRONMENTAL PROTECTION AGENCY

EPA METHOD VALIDATION STUDY-1T ENVIROSCI CHLORCARS

EFFECT OF WATER TYPE ON 1,3-DICHLOROBENZENE ANALYSIS

** POINT ESTIMATES **

DISTILLED WATER SLOPE:GAMMA(1) = .92631

WATER	INTERCEPT(WATER-DISTILLED)	SLOPE(WATER-DISTILLED)
2	.2508	-.0149
3	-.1655	.0731
4	.1979	.0056
5	-.0841	.0404
6	-.0056	.0372

** ANALYSIS OF VARIANCE **

SOURCE	DF	SUM OF SQUARES	MEAN SQUARE	F	PROB
REG(DISTILLED)	1	404.25427	404.25427		
REG(WATER/DISTILLED)	10	3.05644	.30564	2.28	.0130
ERROR	471	63.13714	.13405		
TOTAL	482	470.44785			

** TABLE OF 95% CONFIDENCE INTERVALS FOR THE DIFFERENCES BETWEEN INTERCEPTS AND THE DIFFERENCES BETWEEN SLOPES **

WATER	INTERCEPT(WATER-DISTILLED) ESTIMATE	INTERVAL	SLOPE(WATER-DISTILLED) ESTIMATE	INTERVAL
2	.2508	(-.4642 , .9657)	-.0149	(-.1809 , .1511)
3	-.1655	(-.9045 , .5736)	.0731	(-.0986 , .2447)
4	.1979	(-.5271 , .9230)	.0066	(-.1609 , .1741)
5	-.0841	(-.8070 , .6387)	.0404	(-.1272 , .2081)
6	-.0056	(-.7187 , .7075)	.0372	(-.1282 , .2026)

NOTE: IF ZERO IS CONTAINED WITHIN A GIVEN CONFIDENCE INTERVAL THEN THERE IS NO STATISTICAL SIGNIFICANCE BETWEEN DISTILLED WATER AND THE CORRESPONDING WASTE WATER FOR THE ASSOCIATED PARAMETER(INTERCEPT/SLOPE).

THE SLOPE AND INTERCEPT ESTIMATES FROM THIS ANALYSIS ARE NOT THE SAME AS THOSE OBTAINED FROM THE PRECISION AND ACCURACY REGRESSIONS PERFORMED EARLIER.

TABLE A-34.

ENVIRONMENTAL MONITORING AND SUPPORT LABORATORY
OFFICE OF RESEARCH AND DEVELOPMENT
ENVIRONMENTAL PROTECTION AGENCY

EPA METHOD VALIDATION STUDY-IT ENVIROSCI CHTDRCARS

EFFECT OF WATER TYPE ON 1,4-DICHLOROBENZENE ANALYSIS

** POINT ESTIMATES **

DISTILLED WATER SLOPE:GAMMA(1) = .92055

WATER	INTERCEPT(WATER-DISTILLED)	SLOPE(WATER-DISTILLED)
2	-.2331	.0612
3	.2724	-.0440
4	-.5122	.1172
5	-.2937	.0653
6	-.0142	.0211

** ANALYSIS OF VARIANCE **

SOURCE	DF	SUM OF SQUARES	MEAN SQUARE	F	PROB
REG(DISTILLED)	1	594.50214	594.50214		
REG(WATER/DISTILLED)	10	2.26909	.22691	1.22	.2776
ERROR	535	99.84706	.18663		
TOTAL	546	696.61830			

** TABLE OF 95% CONFIDENCE INTERVALS FOR THE DIFFERENCES BETWEEN INTERCEPTS AND THE DIFFERENCES BETWEEN SLOPES **

WATER	INTERCEPT(WATER-DISTILLED) ESTIMATE	INTERVAL	SLOPE(WATER-DISTILLED) ESTIMATE	INTERVAL
2	-.2331	(-1.0334 , .5672)	.0612	(-.1035 , .2259)
3	.2724	(-.4977 , 1.0425)	-.0440	(-.2026 , .1145)
4	-.5122	(-1.3112 , .2868)	.1172	(-.0466 , .2810)
5	-.2937	(-1.0981 , .5106)	.0653	(-.0994 , .2300)
6	-.0142	(-.8249 , .7965)	.0211	(-.1445 , .1867)

NOTE: IF ZERO IS CONTAINED WITHIN A GIVEN CONFIDENCE INTERVAL THEN THERE IS NO STATISTICAL SIGNIFICANCE BETWEEN DISTILLED WATER AND THE CORRESPONDING WASTE WATER FOR THE ASSOCIATED PARAMETER(INTERCEPT/SLOPE).

THE SLOPE AND INTERCEPT ESTIMATES FROM THIS ANALYSIS ARE NOT THE SAME AS THOSE OBTAINED FROM THE PRECISION AND ACCURACY REGRESSIONS PERFORMED EARLIER.

TABLE A-35.

ENVIRONMENTAL MONITORING AND SUPPORT LABORATORY
OFFICE OF RESEARCH AND DEVELOPMENT
ENVIRONMENTAL PROTECTION AGENCY

EPA METHOD VALIDATION STUDY-IT ENVIROSCI CHTDRCARS

EFFECT OF WATER TYPE ON 1,2,4-TRICHLOROBENZENE ANALYSIS

** POINT ESTIMATES **

DISTILLED WATER SLOPE:GAMMA(1) = .91225

WATER	INTERCEPT(WATER-DISTILLED)	SLOPE(WATER-DISTILLED)
2	-.0971	.0313
3	.1660	-.0312
4	-.0686	.0279
5	-.2437	.0710
6	.0934	.0087

** ANALYSIS OF VARIANCE **

SOURCE	DF	SUM OF SQUARES	MEAN SQUARE	F	PROB
REG(DISTILLED)	1	490.16159	490.16159		
REG(WATER/DISTILLED)	10	1.31895	.13189	.98	.4621
ERROR	494	66.66320	.13495		
TOTAL	505	558.14374			

** TABLE OF 95% CONFIDENCE INTERVALS FOR THE DIFFERENCES BETWEEN INTERCEPTS AND THE DIFFERENCES BETWEEN SLOPES **

WATER	INTERCEPT(WATER-DISTILLED) ESTIMATE	INTERVAL	SLOPE(WATER-DISTILLED) ESTIMATE	INTERVAL
2	-.0971	(-.7034 , .5091)	.0313	(-.1183 , .1808)
3	.1660	(-.4375 , .7696)	-.0312	(-.1796 , .1172)
4	-.0686	(-.6657 , .5284)	.0279	(-.1183 , .1742)
5	-.2437	(-.8652 , .3779)	.0710	(-.0808 , .2229)
6	.0934	(-.5217 , .7085)	.0087	(-.1421 , .1595)

NOTE: IF ZERO IS CONTAINED WITHIN A GIVEN CONFIDENCE INTERVAL THEN THERE IS NO STATISTICAL SIGNIFICANCE BETWEEN DISTILLED WATER AND THE CORRESPONDING WASTE WATER FOR THE ASSOCIATED PARAMETER(INTERCEPT/SLOPE).

THE SLOPE AND INTERCEPT ESTIMATES FROM THIS ANALYSIS ARE NOT THE SAME AS THOSE OBTAINED FROM THE PRECISION AND ACCURACY REGRESSIONS PERFORMED EARLIER.

TABLE A-36.

ENVIRONMENTAL MONITORING AND SUPPORT LABORATORY
OFFICE OF RESEARCH AND DEVELOPMENT
ENVIRONMENTAL PROTECTION AGENCY

EPA METHOD VALIDATION STUDY-IT ENVIROSCI CHLORCARS

EFFECT OF WATER TYPE ON HEXACHLOROBENZENE ANALYSIS

** POINT ESTIMATES **

DISTILLED WATER SLOPE:GAMMA(1) = 95414

WATER	INTERCEPT(WATER-DISTILLED)	SLOPE(WATER-DISTILLED)
2	-.0334	.0566
3	.0383	.0603
4	.0946	.0028
5	.0135	.0428
6	-.0359	.0177

** ANALYSIS OF VARIANCE **

SOURCE	DF	SUM OF SQUARES	MEAN SQUARE	F	PROB
REG(DISTILLED)	1	486.36606	486.36606		
REG(WATER/DISTILLED)	10	1.68808	.16881	1.59	.1060
ERROR	511	54.23727	.10614		
TOTAL	522	542.29141			

** TABLE OF 95% CONFIDENCE INTERVALS FOR THE DIFFERENCES BETWEEN INTERCEPTS AND THE DIFFERENCES BETWEEN SLOPES **

WATER	INTERCEPT(WATER-DISTILLED) ESTIMATE	INTERCEPT(WATER-DISTILLED) INTERVAL	SLOPE(WATER-DISTILLED) ESTIMATE	SLOPE(WATER-DISTILLED) INTERVAL
2	-.0334	(-.2999 , .2332)	.0566	(-.0840 , .1973)
3	.0383	(-.2320 , .3086)	.0603	(-.0827 , .2033)
4	.0946	(-.1773 , .3665)	.0028	(-.1395 , .1450)
5	.0135	(-.2574 , .2843)	.0428	(-.0990 , .1846)
6	-.0359	(-.3071 , .2352)	.0177	(-.1244 , .1599)

NOTE: IF ZERO IS CONTAINED WITHIN A GIVEN CONFIDENCE INTERVAL THEN THERE IS NO STATISTICAL SIGNIFICANCE BETWEEN DISTILLED WATER AND THE CORRESPONDING WASTE WATER FOR THE ASSOCIATED PARAMETER(INTERCEPT/SLOPE).

THE SLOPE AND INTERCEPT ESTIMATES FROM THIS ANALYSIS ARE NOT THE SAME AS THOSE OBTAINED FROM THE PRECISION AND ACCURACY REGRESSIONS PERFORMED EARLIER.

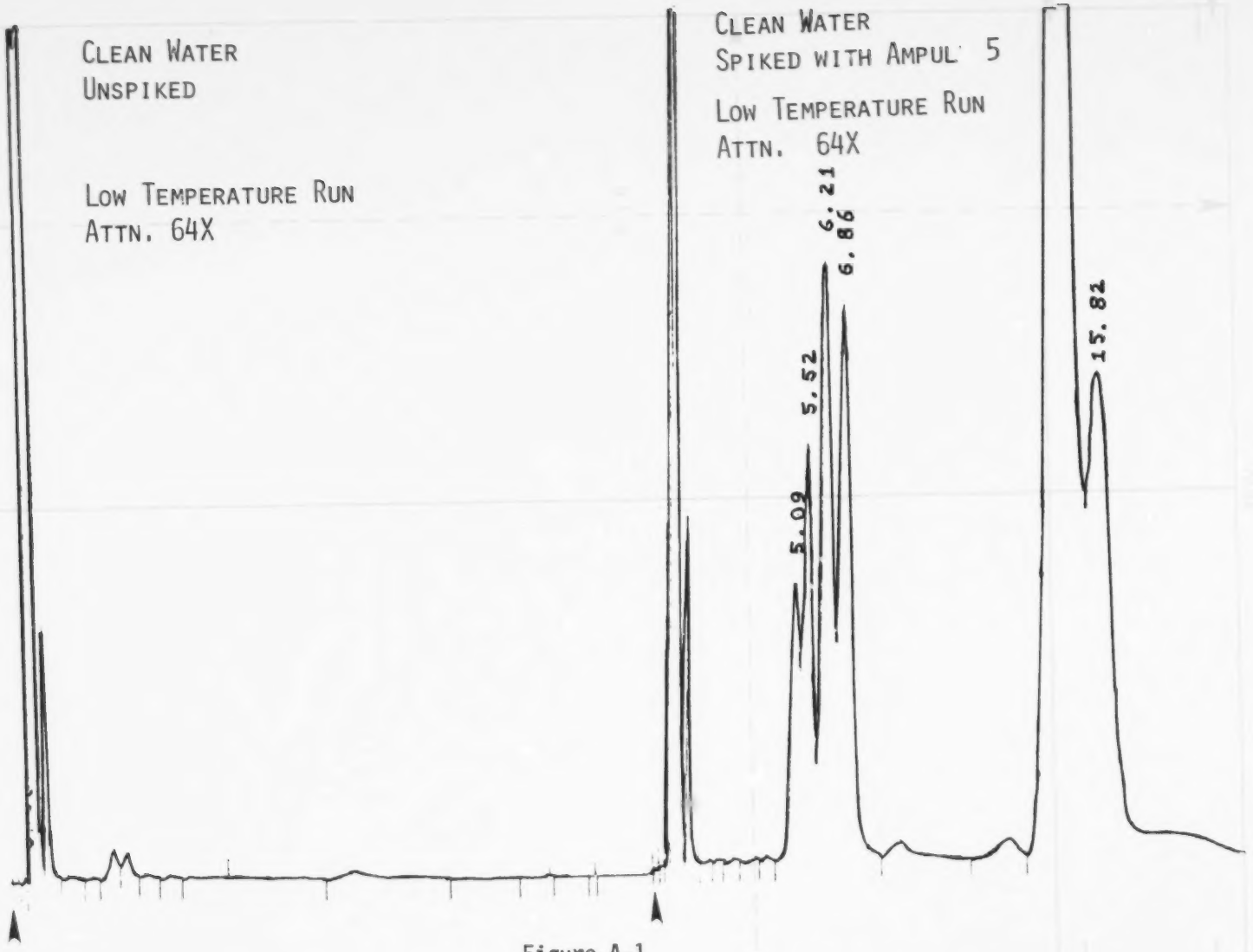

CLEAN WATER
UNSPIKED
LOW TEMPERATURE RUN
ATTN. 64X
CLEAN WATER
SPIKED WITH AMPUL 5
LOW TEMPERATURE RUN
ATTN. 64X
5.09
5.52
6.86
6.21
15.82

Figure A-1

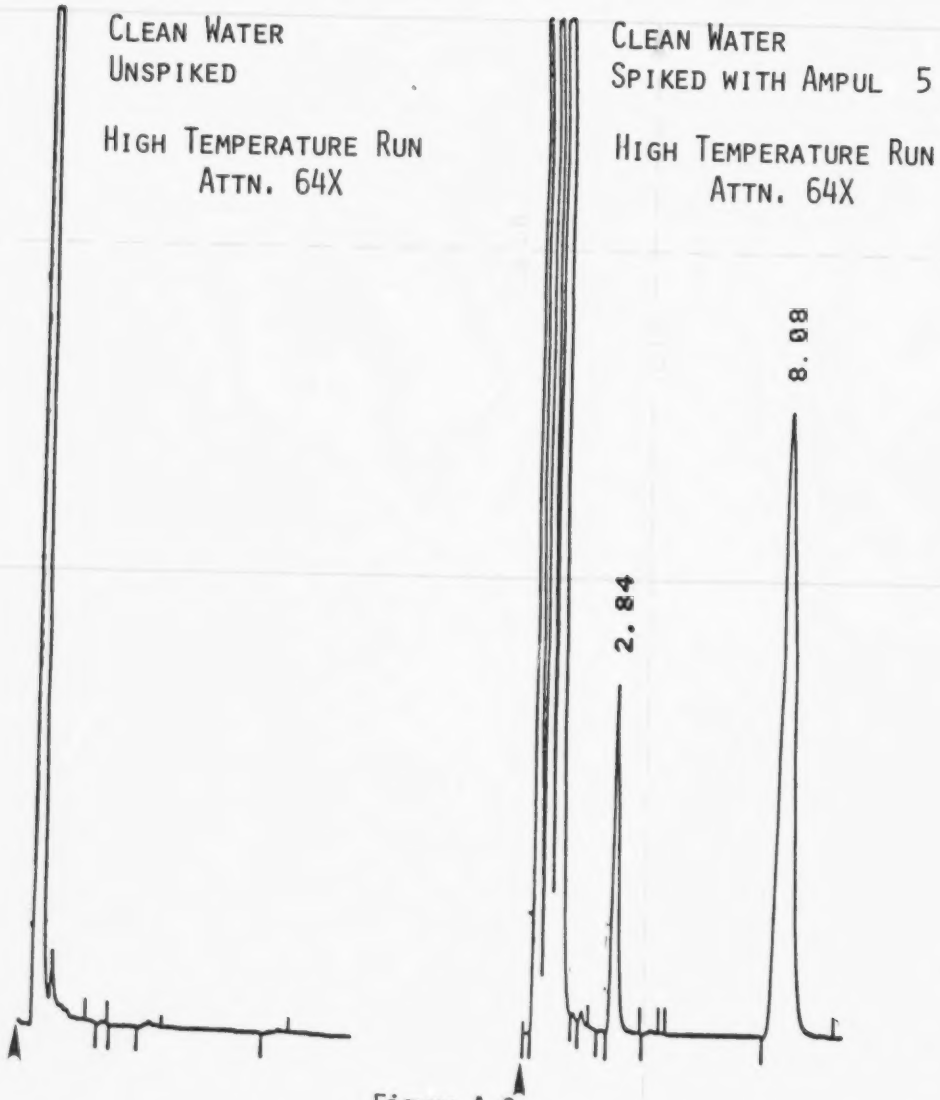

CLEAN WATER
UNSPIKED
HIGH TEMPERATURE RUN
ATTN. 64X
CLEAN WATER
SPIKED WITH AMPUL 5
HIGH TEMPERATURE RUN
ATTN. 64X
8.08
2.84

Figure A-2

WASTEWATER No. 1
UNSPIKED
LOW TEMPERATURE RUN
7.04
18.30
19.68
HR

Figure A-3

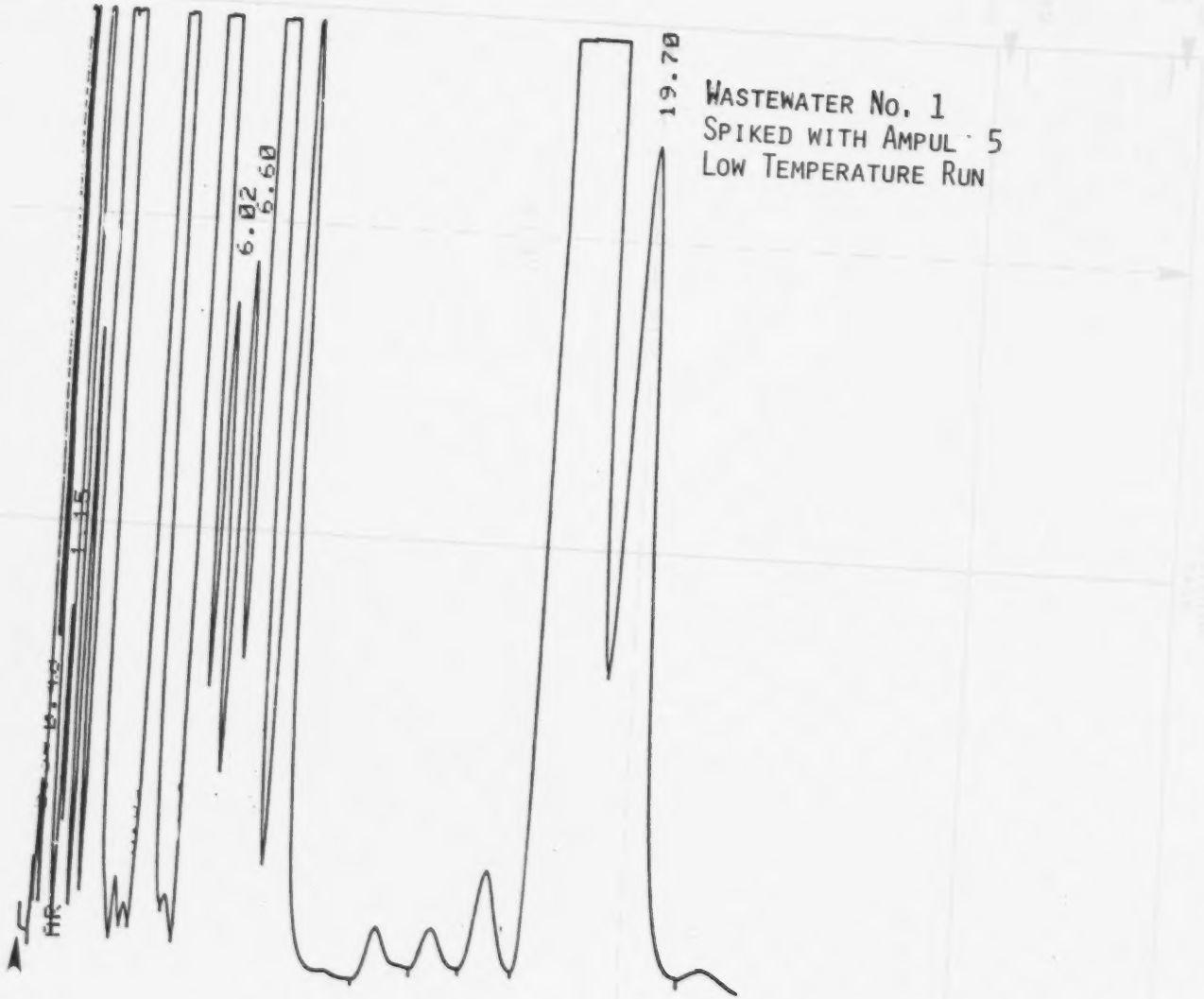

19.70
6.02
6.60
1.15
WASTEWATER No. 1
SPIKED WITH AMPUL 5
LOW TEMPERATURE RUN

Figure A-4

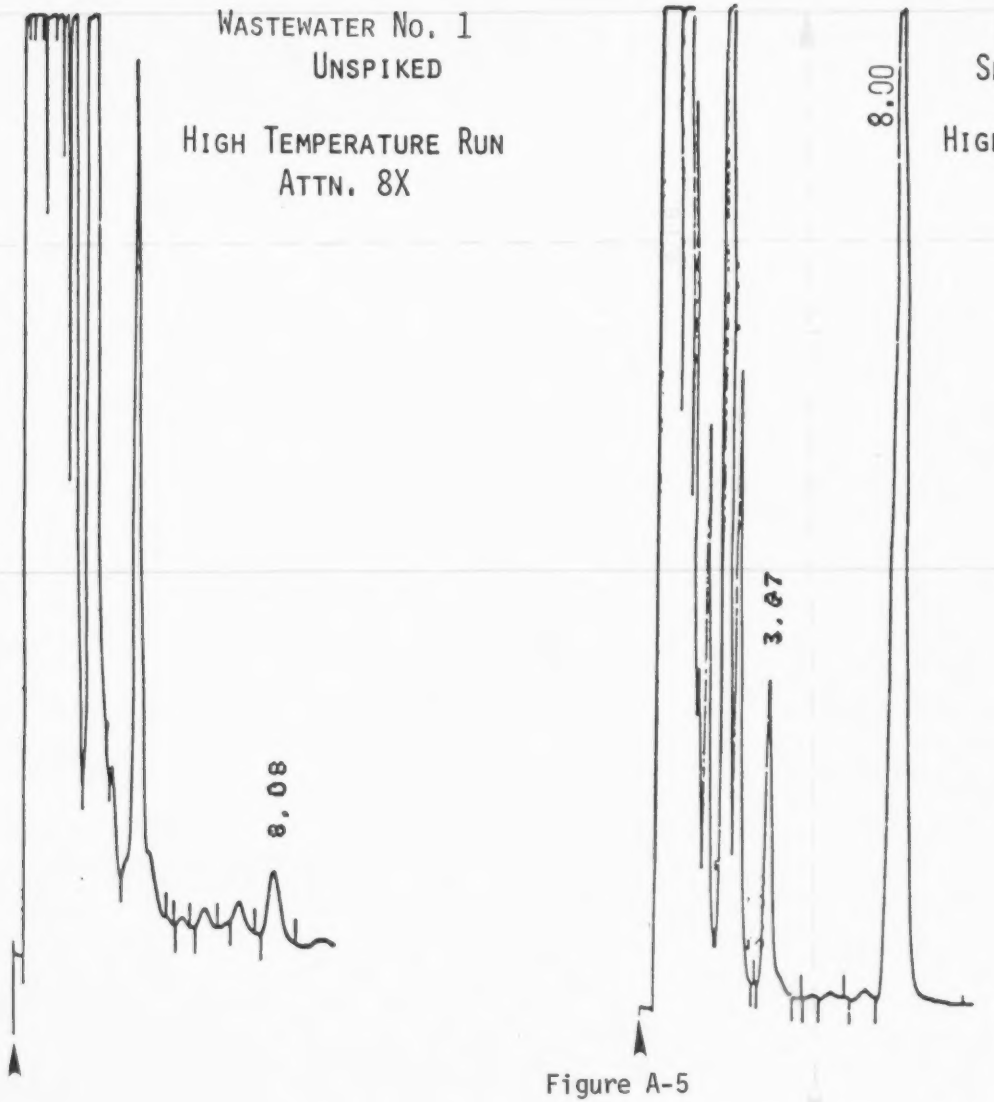

WASTEWATER No. 1
UNSPIKED
HIGH TEMPERATURE RUN
ATTN. 8X
8.08
WASTEWATER No. 1
SPIKED WITH AMPUL 2
HIGH TEMPERATURE RUN
ATTN. 64X
8.00
3.67

Figure A-5

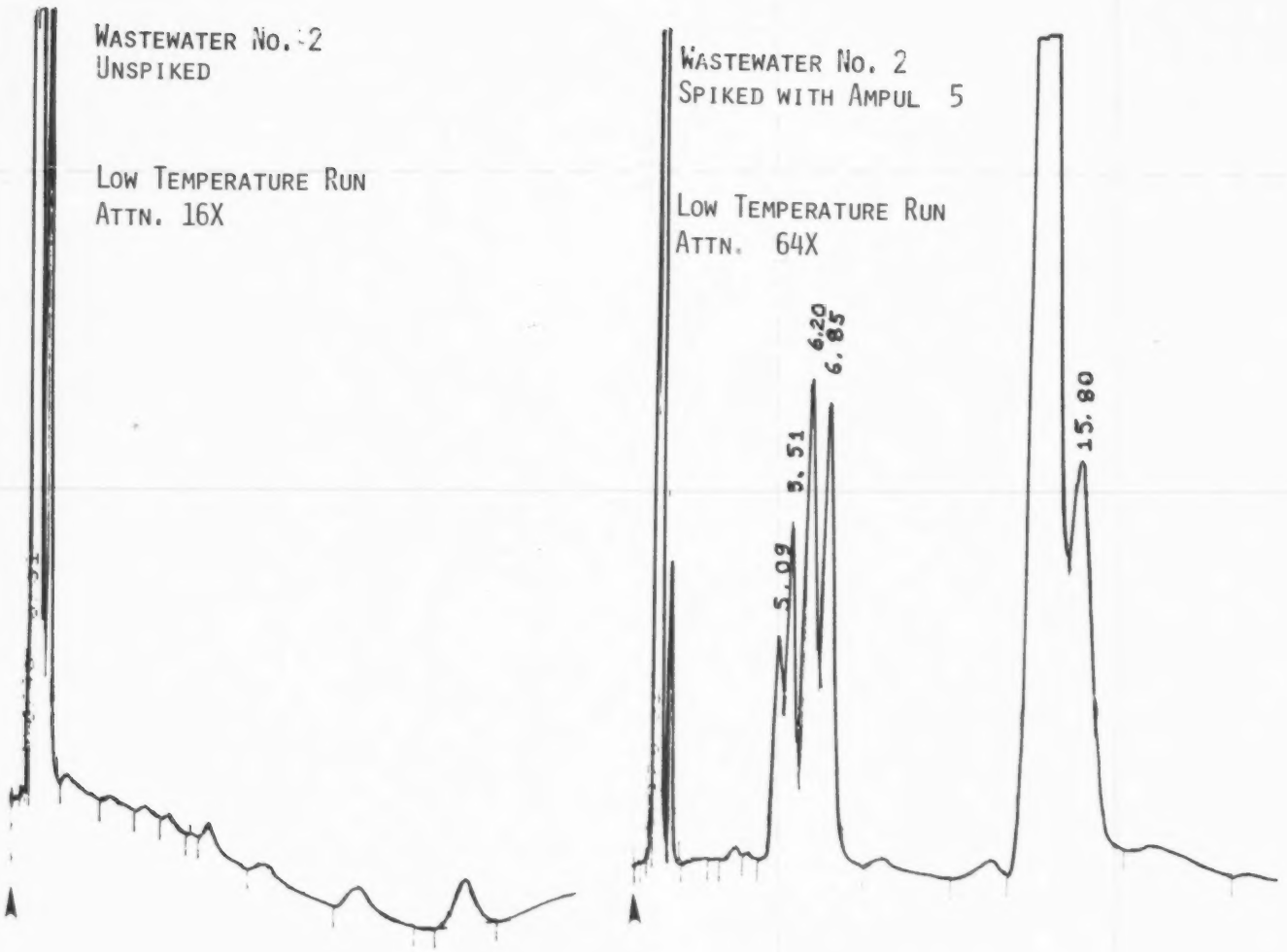

WASTEWATER No. 2
UNSPIKED
LOW TEMPERATURE RUN
ATTN. 16X
WASTEWATER No. 2
SPIKED WITH AMPUL 5
LOW TEMPERATURE RUN
ATTN. 64X
5.09
5.51
6.20
6.85
15.80

Figure A-6

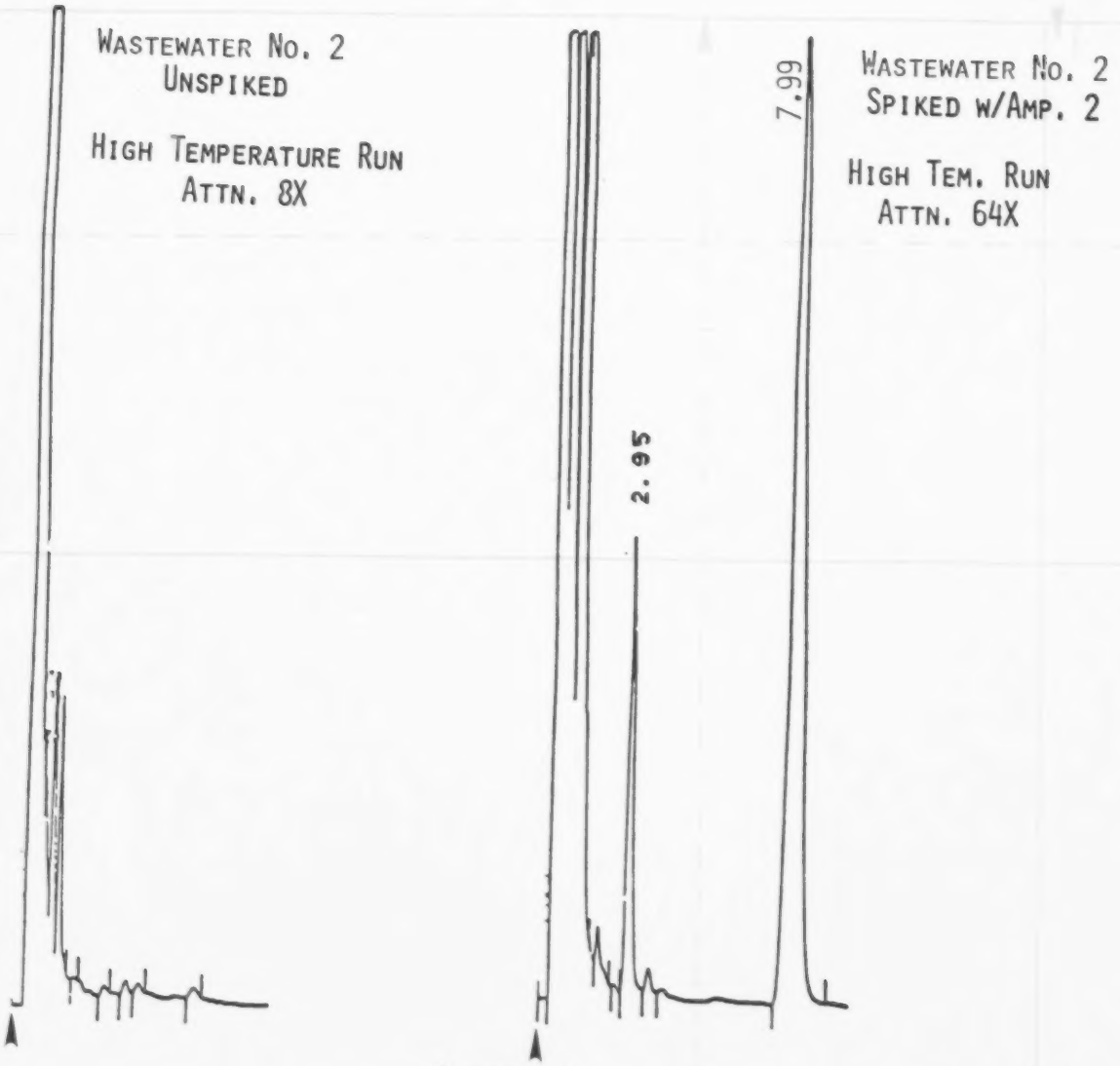

WASTEWATER No. 2
UNSPIKED
HIGH TEMPERATURE RUN
ATTN. 8X
WASTEWATER No. 2
SPIKED w/AMP. 2
HIGH TEM. RUN
ATTN. 64X
7.99
2.95

Figure A-7

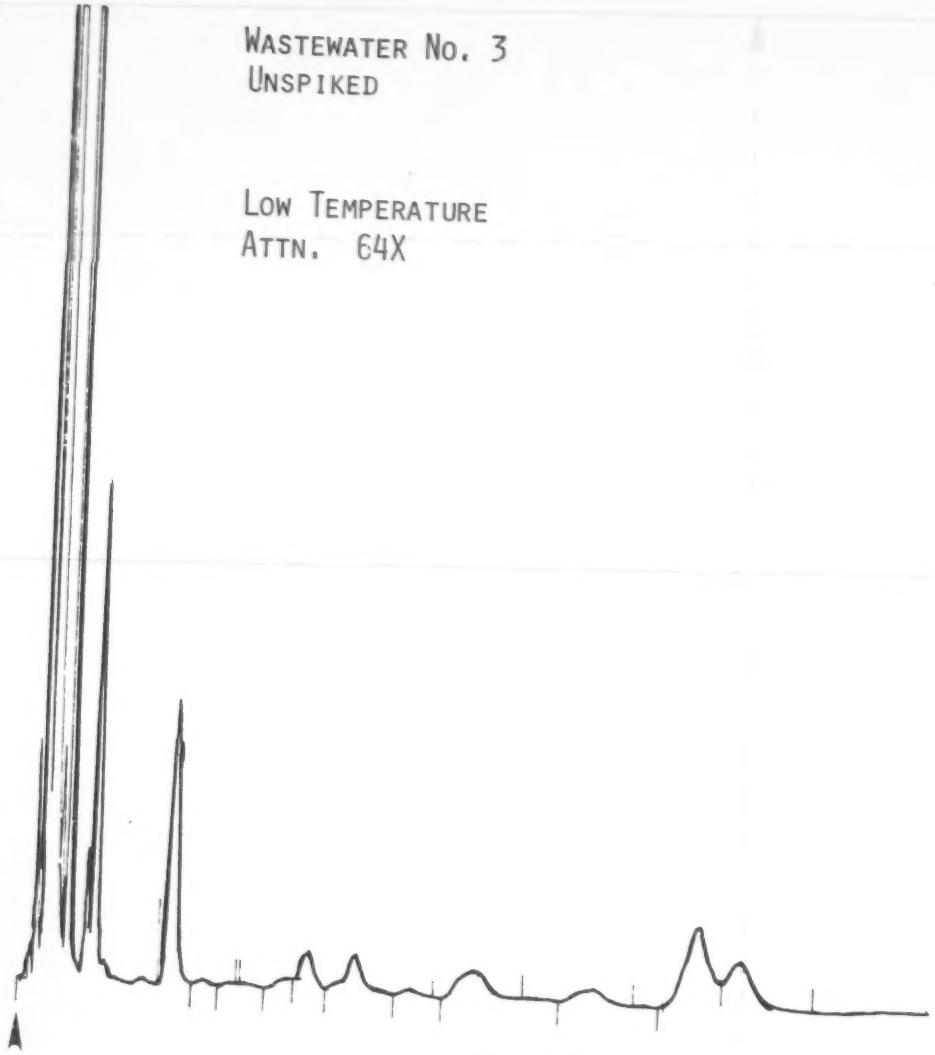
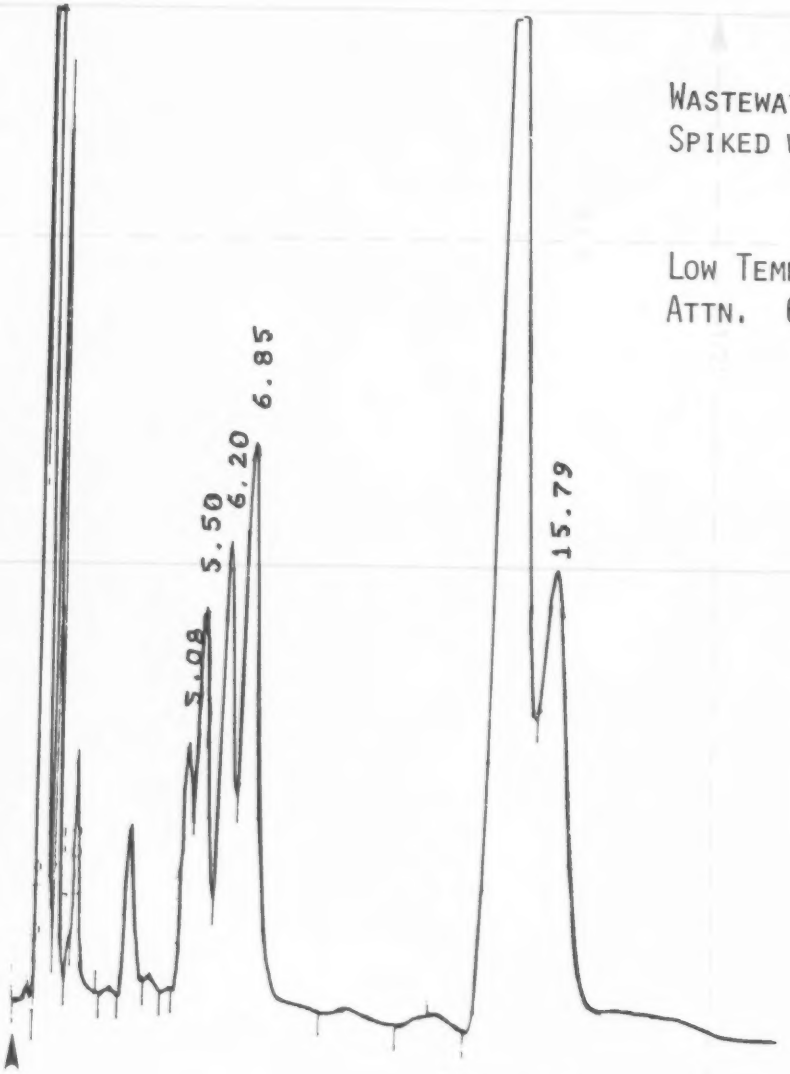


Figure A-8



WASTEWATER NO. 3
SPIKED WITH AMPUL 5

LOW TEMPERATURE RUN
ATTN. 64X

Figure A-9

WASTEWATER NO. 3
UNSPIKED
HIGH TEMPERATURE RUN
ATTN. 8X
2.84
8.08

WASTEWATER NO. 3
SPIKED WITH AMPUL 2
HIGH TEMPERATURE RUN
ATTN. 64X
2.85
8.09

Figure A-10

APPENDIX B

CHLORINATED HYDROCARBONS: ANALYTICAL METHOD 612

1. Scope and Application

1.1 This method covers the determination of certain chlorinated hydrocarbons. The following parameters may be determined by this method:

Parameter	STORET No.
Hexachlorocyclopentadiene	34386
Hexachlorobenzene	39700
Hexachlorobutadiene	34391
Hexachloroethane	34396
1,2-Dichlorobenzene	34536
1,2,4-Trichlorobenzene	34551
1,3-Dichlorobenzene	34566
1,4-Dichlorobenzene	34571
2-Chloronapthalene	34581

1.2 This method is applicable to the determination of these compounds in municipal and industrial discharges. It is designed to be used to meet the monitoring requirements of the National Pollutant Discharge Elimination System (NPDES). As such, it presupposes a high expectation of finding the specific compounds of interest. If the user is attempting to screen samples for any or all the compounds above, he must develop independent protocols for the verification of identity.

1.3 The sensitivity of this method is usually dependent on the level of interferences rather than instrumental limitations. The limits of detection listed in Table 1 represent sensitivities that can be achieved in wastewaters in the absence of interferences.

1.4 This method is recommended for use only by experienced residue analysts or under the close supervision of such qualified persons.

2. Summary of Method

2.1 A 1 liter sample of wastewater is extracted with methylene chloride using separatory funnel techniques. The extract is dried by passing through a sodium sulfate column and then

concentrated to a volume of 10 mL or less. Chromatographic conditions are described which allow for the accurate measurement of the compounds in the extract.

2.2 If interferences are encountered or expected, the method provides a selected general purpose clean up procedure to aid the analyst in eliminating them.

3. Interferences

3.1 Solvents, reagents, glassware, and other sample processing hardware may yield discrete artifacts and/or elevated baselines causing misinterpretation of gas chromatograms. All of these materials must be demonstrated to be free from interferences under the conditions of the analysis by running method blanks. Specific selection of reagents and purification of solvents by distillation in all glass systems may be required.

3.2 Interferences coextracted from the samples will vary considerably from source to source, depending on the diversity of the industrial complex or municipality being sampled. While general clean up techniques are provided as part of this method, unique samples may require additional clean up approaches to achieve the sensitivities stated in Table 1.

4. Apparatus and Materials

4.1 Sampling equipment, for discrete or composite sampling.

4.1.1 Grab sample bottle - Amber glass, 1 liter or 1 quart volume. French or Boston Round design is recommended. The container must be washed and rinsed with solvent before use to minimize interferences.

4.1.2 Bottle caps - Threaded to screw on sample bottles. Caps must be lined with Teflon. Foil may be substituted if sample is not corrosive and foil is found to be interference free.

4.1.3 Compositing equipment - Automatic or manual compositing system. Must incorporate glass sample containers for the collection of a minimum of 250 mL. Sample containers must be kept refrigerated during sampling. No tygon or rubber tubing or fittings may be used in the system.

4.2 Separatory funnel - 2000 mL, with Teflon stopcock.

4.3 Drying column - 20 mm ID pyrex chromatographic column with coarse frit.

4.4 Kuderna-Danish (K-D) Apparatus

4.4.1 Concentrator tube - 10 mL, graduated (Kontes K-570050-1025 or equivalent). Calibration must be checked. Ground glass stopper (size 19/22 joint) is used to prevent evaporation of extracts.

4.4.2 Evaporative flask - 500 mL (Kontes K-47001-0500 or equivalent). Attach to concentrator tube with springs. (Kontes K-662750-0012).

4.4.3 Snyder column - three-ball macro (Kontes K-503000-0121 or equivalent).

4.4.4 Snyder column - two-ball micro (Kontes K-569001-0219 or equivalent).

4.4.5 Boiling chips - solvent extracted, approximately 10/40 mesh.

4.5 Water bath - Heated, with concentric ring cover, capable of temperature control (±2°C). The bath should be used in a hood.

4.6 Gas chromatograph - Analytical system complete with gas chromatograph suitable for on column injection and all required accessories including electron capture detector, column supplies, recorder, gasses, syringes. A data system for measuring peak areas is recommended.

4.7 Chromatography column - 300 mm long X 10 mm ID with coarse fritted disc at bottom and Teflon stopcock.

5. Reagents

5.1 Preservatives

5.1.1 Sodium hydroxide - (ACS) 10 N in distilled water.

5.1.2 Sulfuric acid - (ACS) Mix equal volumes of concentrated H_2SO_4 with distilled water.

5.2 Methylene chloride, hexane and petroleum ether (boiling range 30 to 60°C) - Pesticide quality or equivalent.

5.3 Sodium sulfate - (ACS) Granular, anhydrous (purified by heating at 400°C for 4 hr in a shallow tray).

5.4 Stock standards - Prepare stock standard solutions at a concentration of 1.00 µg/µL by dissolving 0.100 grams of assayed reference material in pesticide quality hexane or other appropriate solvent and diluting to volume in a 100 mL ground

glass stoppered volumetric flask. The stock solution is transferred to ground glass stoppered reagent bottles, stored in a refrigerator, and checked frequently for signs of degradation or evaporation, especially just before preparing working standards from them.

5.5 Florisil - PR grade (60/100 mesh): purchase activated at 1250°F and store in the dark in glass containers with glass stoppers or foil-lined screw caps. Before use, activate each batch at 130°C in foil-covered glass containers.

6. Calibration

6.1 Prepare calibration standards that contain the compounds of interest, either singly or mixed together. The standards should be prepared at concentrations covering two or more orders of magnitude that will completely bracket the working range of the chromatographic system. If the sensitivity of the detection system can be calculated from Table A-1 as 100µg/L in the final extract, for example, prepare standards at 10 µg/L, 50 µg/L, 100 µg/L, 500 µg/L, etc. so that injections of 1 to 5 µL of each calibration standard will define the linearity of the detector in the working range.

6.2 Assemble the necessary gas chromatographic apparatus and establish operating parameters equivalent to those indicated in Table A-1. By injecting calibration standards, establish the sensitivity limit of the detector and the linear range of the analytical system for each compound.

6.3 The clean up procedure in Section 10 utilizes Florisil chromatography. Florisil from different batches or sources may vary in absorption capacity. To standardize the amount of Florisil that is used, the use of lauric acid value (Mills, 1968) is suggested. The referenced procedure determines the adsorption from hexane solution of lauric acid (mg) per gram Florisil. The amount of Florisil to be used for each column is calculated by dividing this ratio by 110 and multiplying by 20 grams.

6.4 Before using any clean up procedure, the analyst must process a series of calibration standards through the procedure to validate elution patterns and the absence of interferences from the reagents.

7. Quality Control

7.1 Before processing any samples the analyst should demonstrate, through the analysis of a distilled water method blank, that all glassware and reagents are free of interference. Each time a set of samples is extracted or there is a change in reagents, a method blank should be processed as a safeguard against chronic laboratory contamination.

7.2 Standard quality assurance practices should be used with this method. Field replicates should be collected to validate the accuracy of the analysis. Where doubt exists over the identification of a peak on the chromatogram, confirmatory techniques such as mass spectroscopy should be used.

8. Sample Collection, Preservation, and Handling

8.1 Grab samples must be collected in glass containers, leaving a minimum headspace. Conventional sampling practices should be followed, except that the bottle must not be prewashed with sample before collection. Composite samples should be collected in refrigerated glass containers in accordance with the requirements of the program. Automatic sampling equipment must be free of tygon and other potential sources of contamination.

8.2 The samples must be iced or refrigerated from the time of collection until extraction. Chemical preservatives should not be used in the field unless more than 24 hours will elapse before delivery to the laboratory. If the samples will not be extracted within 48 hours of collection, they should be adjusted to a pH range of 6.0 to 8.0 with sodium hydroxide or sulfuric acid.

8.3 All samples should be extracted immediately and must be extracted within 7 days and completely analyzed within 30 days after collection.

9. Sample Extraction

9.1 Mark the water meniscus on the side of the sample bottle for later determination of sample volume. Pour the entire sample into a two liter separatory funnel. Check the pH of the sample with wide range paper and adjust to within the range of 5 to 9 with sodium hydroxide or sulfuric acid.

9.2 Add 60 mL methylene chloride to the sample bottle, seal and shake 30 seconds to rinse the inner walls. Transfer the solvent into the separatory funnel, and extract the sample by shaking the funnel for two minutes with periodic venting to release vapor pressure. Allow the organic layer to separate from the water phase for a minimum of ten minutes. If the emulsion interface between layers is more than one-third the size of the solvent layer, the analyst must employ mechanical techniques to complete the phase separation. The optimum technique depends on the sample, but may include stirring, filtration of the emulsion through glass wool, or centrifugation. Collect the methylene chloride extract in a 250 mL Ehrlenmeyer flask.

9.3 Add a second 60 ml volume of methylene chloride to the sample bottle and complete the extraction procedure a second time, combining the extracts in the Ehrlenmeyer flask.

9.4 Perform a third extraction in the same manner. Pour the combined extract through a drying column containng 3 to 4 inches of anhydrous sodium sulfate, and collect it in a 500 mL Kuderna-Danish (K-D) flask equipped with a 10 mL concentrator tube. Rinse the Erhlenmeyer flask and column with 20 to 30 mL methylene chloride to complete the quantitative transfer.

9.5 Add 1 to 2 clean boiling chips to the flask and attach a three ball Snyder column. Prewet the Snyder column by adding about 1 mL methylene chloride to the top. Place the K-D apparatus on a hot water bath (60 to 65°C) so that the concentrator tube is partially immersed in the hot water and the entire lower rounded surface of the flask is bathed in vapor. Adjust the vertical position of the apparatus and the water temperature as required to complete the concentration in 15 to 20 minutes. At the proper rate of distillation the balls of the column will actively chatter but the chambers will not flood. When the apparent volume of liquid reaches 1 to 2 mL, remove the K-D apparatus and allow it to drain for at least 10 minutes while cooling. Note -- The dichlorobenzenes have a sufficiently high volatility that significant losses may occur in concentration steps if care is not exercised. It is important to maintain a constant gentle evaporation rate and not to allow the liquid volume to fall below 1 to 2 mL before removing the K-D from the hot water bath.

9.6 Momentarily remove the Snyder column, add 50 ml hexane and a new boiling chip and replace the column. Raise the temperature of the water bath to 85 to 90°C. Concentrate the extract as in 9.5, except use hexane to prewet the column. Remove the Snyder column and rinse the flask and its lower joint into the concentrator tube with 102 mL of hexane. A 5 mL syringe is recommended for this operation. Stopper the concentrator tube and refrigerate if further processing will not be performed immediately.

9.7 Determine the original sample volume by refilling the sample bottle to the mark and transferring the liquid to a 1000 mL graduated cylinder. Record the sample volume to the nearest 5 mL.

9.8 Unless the sample is known to require clean up, proceed to analysis by gas chromatography.

10. Clean up and Separation

10.1 Florisil Column Clean up for Chlorinated Hydrocarbons.

10.1.1 Adjust the sample extract to 10 mL.

10.1.2 Place a 12 gram charge of activated Florisil (see 6.3) in a 10 mm ID chromatography column. After settling the Florisil by tapping the column, add a 1 to 2 cm layer of anhydrous granular sodium sulfate to the top.

10.1.3 Pre-elute the column, after cooling, with 100 mL of petroleum ether. Discard the eluate and just before exposure of the sulfate layer to air, quantitatively transfer the sample extract into the column by decantation and subsequent petroleum ether washings. Discard the eluate. Just before exposure of the sodium sulfate layer to the air, begin eluting the column with 200 mL petroleum ether and collect the eluate in a 500 mL K-D flask equipped with a 10 mL concentrator tube. This fraction should contain all of the chlorinated hydrocarbons.

10.1.4 Concentrate the fraction by K-D as in 9.5 except prewet the column with hexane. When the apparatus is cool, remove the Snyder column and rinse the flask and its lower joint into the concentrator tube with 1 to 2 mL hexane. Analyze by gas chromatography.

11. Gas Chromatography

11.1. Table 1 summarizes some recommended gas chromatographic column materials and operating conditions for the instrument. Included in this table are estimated retention times and sentitivities that should be achieved by this method. Examples of the separations achieved by this column are shown in Figs. 1 and 2. Calibrate the system daily with a minimum of three injections of calibration standards.

TABLE 1. GAS CHROMATOGRAPHY OF CHLORINATED HYDROCARBONS

Compound	Retention Time (Minutes)	Detection Limit† (µg/L)
1,3-Dichlorobenzene	5.6	0.009
1,4-Dichlorobenzene	6.1	0.018
Hexachloroethane	6.7	0.001
1,2-Dichlorobenzene	7.6	0.012
Hexachlorobutadiene	15.8	0.001
1,2,4-Trichlorobenzene	17.7	0.006
Hexachlorocyclopentadiene	2.0*	0.001
2-Chloronaphthalene	3.65*	0.015
Hexachlorobenzene	10.3*	0.001

Column conditions: Supelcoport 80/100 mesh coated with 1.5% OV-1/2.4% OV-225 packed in a 1.8 m long X 2 MM ID glass column with 5% methane/95% argon carrier gas at 30 mL/min flow rate. Column temperature is 75°C except where * indicates 165°C. Under these conditions R.T. of Aldrin is 27.4 minutes at 160°C.

†Detection limit is calculated from the minimum detectable GC response of the electron capture detector being equal to five times the GC background noise, assuming a 10 mL final volume of the 1 liter sample extract, and assuming a GC injection of 5 microliters.

11.2 Inject 2 to 5 µL of the sample extract using the solvent-flush technique. Smaller (1.0 µL) volumes can be injected if automatic devices are employed. Record the volume injected to the nearest 0.05 µL, and the resulting peak size, in area units.

11.3 If the peak area exceeds the linear range of the system, dilute the extract and reanalyze.

11.4 If the peak area measurement is prevented by the presence of interferences, further clean up is required.

12. Calculations

12.1 Determine the concentration of individual compounds according to the formula:

$$\text{Concentration, } \mu g/L = \frac{(A)\ (B)\ (V_t)}{(V_i)\ (V_s)}$$

Where: A = Calibration factor for chromatographic system, in nanograms material per area unit

B = Peak size in injection of sample extract, in area units

V_i = Volume of extract injected (µL)

V_t = Volume of total extract (µL)

V_s = Volume of water extracted (mL)

12.2 Report results in micrograms per liter without correction for recovery data. When duplicate and spiked samples are analyzed, all data obtained should be reported.

13. Accuracy and Precision

The U.S. EPA Environmental Monitoring and Support Laboratory in Cincinnati is in the process of conducting an interlaboratory method study to determine the accuracy and precision of the test procedure.

COLUMN: 1.5% OV-1+ 2.4% OV-225 ON SUPLECOPORT
TEMPERATURE: 75°C
DETECTOR: ELECTRON CAPTURE

I.D.	COMPOUND
A	1,3-DICHLOROBENZENE
B	1,4-DICHLOROBENZENE
C	HEXACHLOROETHANE
D	1,2-DICHLOROBENZENE
E	HEXACHLOROBUTADIENE
F	1,2,4-TRICHLOROBENZENE

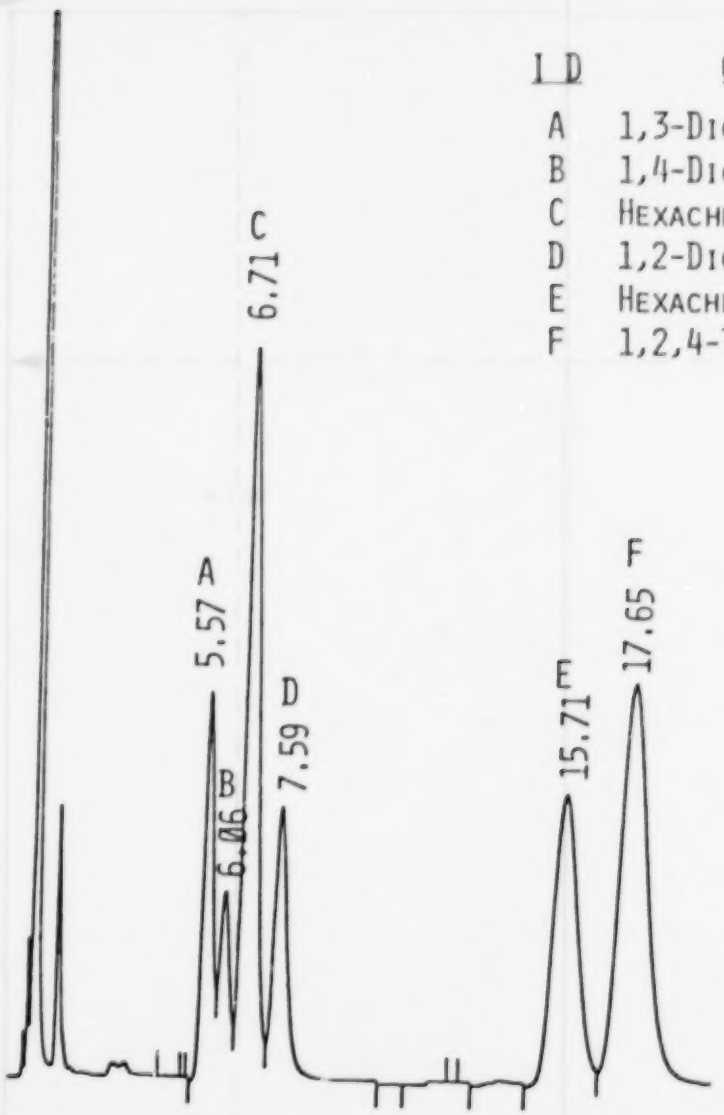
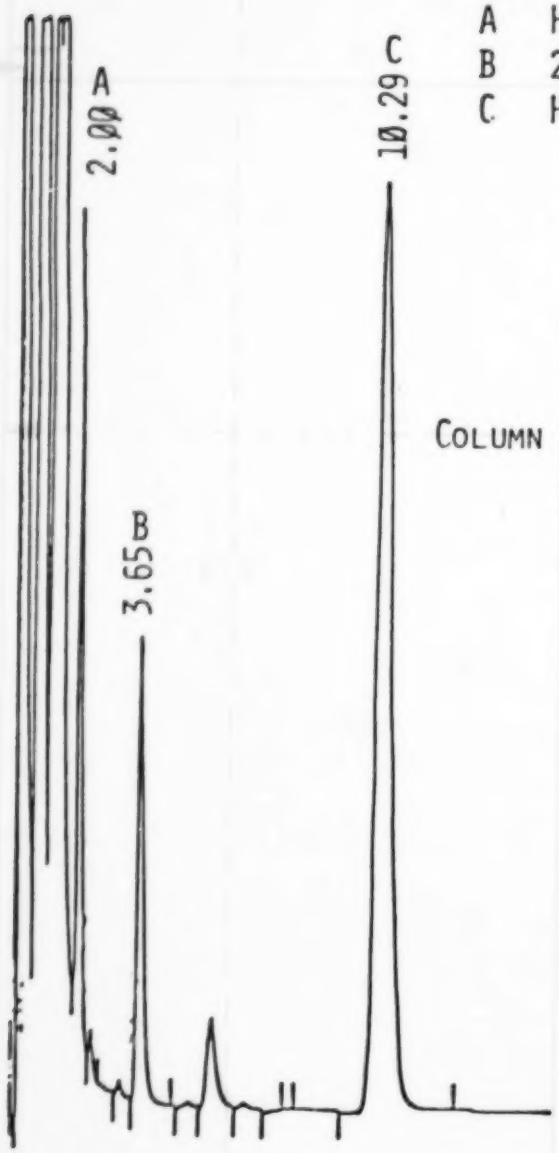


FIGURE 1. GAS CHROMATOGRAM OF CHLORINATED HYDROCARBONS



I D	Compound
A	Hexachlorocyclopentadiene
B	2-Chloronaphthalene
C	Hexachlorobenzene

Column 1.5% OV-1+
2.4% OV-225 on Suplecoport
Temperature: 165°C
Detector: Electron Capture

Figure 2. Gas chromatogram of chlorinated hydrocarbons

REFERENCES

1. Mills, P. A., Variation of Florisil Activity: Simple Method for Measuring Absorbent Capacity and Its Use in Standardizing Florosil Columns, Journal of the Association of Official Analytical Chemists. 29:51, 1968.